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HYDROCHLORIC ACID
AND
SODIUM SULFATE

6008
1425

BY
N. A. LAURY
CONSULTING CHEMICAL ENGINEER

American Chemical Society
Monograph Series

BOOK DEPARTMENT
The CHEMICAL CATALOG COMPANY, *Inc.*
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The object of this monograph is to present the most useful available information in convenient form, without including more of historical value only, than is necessary to trace the evolution of modern equipment. The properties of the compounds are given with such brief explanations as may make them useful to the man in the plant. The discussions of the principles of the processes and apparatus are intended primarily for the needs of the engineer and the manufacturer, and it is hoped also that they may indicate to the chemist and the student those directions in which lie future improvements.

N. A. Laury.

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HYDROCHLORIC ACID AND SODIUM SULFATE

Chapter I

The Action of Sulfuric Acid on Sodium Chloride

Three centuries ago Glauber observed that when sulfuric acid is poured over common salt, even at ordinary temperature, a colorless sharp-smelling gas is evolved. This gas, hydrogen chloride, is readily soluble in water, thus forming the solution with which we are most familiar as hydrochloric, chlorohydric or muriatic acid.

With the exception of a relatively small output of electrolytic hydrochloric acid and an equally small production of natural sodium sulfate, all of our salt cake and hydrochloric acid are made by decomposing salt with sulfuric acid or with sodium bisulfate in a salt cake furnace. The reaction occurs in two steps:

$$NaCl + H_2SO_4 = HCl + NaHSO_4 + 0.8 \text{ calories}$$
$$NaCl + NaHSO_4 = HCl + Na_2SO_4 + 15.0 \text{ calories}$$

Both of these reactions are so slightly exothermic that heat must be applied in practice to carry them to completion at a rapid rate. At room temperature the reaction is not complete, and soon ceases. When the mixture is heated the decomposition proceeds until, if there be sufficient salt present, all of the sulfuric acid is converted into acid sodium sulfate. Any excess of acid when present will remain unaltered. If two molecules of sodium chloride be taken per molecule of sulfuric acid, on heating the mixture to a moderate temperature only one half of the salt will suffer change. Complete decomposition, after which neither hydrogen nor chlorine is left in the residue, proceeds at a red heat only. The second equation results from the action of the acid salt, $NaHSO_4$, first formed, on sodium chloride, for the acid salt, since it contains hydrogen, itself acts like

an acid. Hence, in the above reactions, non-volatile or sparingly volatile salt and sparingly volatile sulfuric acid are taken, and as the result of their reaction, after the hydrogen and sodium have changed places, there is obtained non-volatile sodium sulfate and gaseous hydrochloric acid. The fact that the latter is a gas forms the main reason why the reaction proceeds to the very end, according to Mendeleeff.[1]

Theory of the Reaction

The volatility of the acid is the cause of the progress of the reaction; indeed if the acid were soluble but not volatile, or if the reaction took place in an enclosed space when the resulting acid could not volatilize, or at the ordinary temperature when it would not volatilize, then the decomposition would not proceed to the end, but only up to a certain limit. In this respect the explanations given at the beginning of the nineteenth century by the French chemist Berthollet [2] are very important. The doctrine of Berthollet starts from the supposition that the chemical reaction of substances is determined by the relative masses of the reacting substances and by those physical conditions under which the reaction takes place. The influence of mass on the amount of decomposition forms the root of Berthollet's doctrine. Another most important principle of his teaching is the attainment of a state of equilibrium.

A very important epoch in the history of Berthollet's doctrine was attained when, in 1867, the Norwegian chemists, Guldberg and Waage, expressed it as an algebraical formula. They defined the active mass as the number of molecules contained in a given volume, and assumed, as follows from the spirit of Berthollet's teaching, that the action between the substances was equal to the product of the masses of the reacting substances. Hence if the reacting substances be taken in equivalent quantities ($M = 1$ and $N = 1$) and two other substances proceed from the mixture, then if k represents the coefficient of the rate of action of the first pair and k_1 the coefficient of the second, then at the moment when the decomposition equals X the measure of action for the first pair is: $k(1 - X)$

[1] "The Principles of Chemistry."
[2] Essai de Statique Chimique.

$(1 - X)$ and for the second pair $k_1 X X_1$, and a state of equilibrium or limit will be reached when $k(1 - X)^2 = k_1 X^2$, whence the ratio

$$\frac{k}{k_1} = \left(\frac{X}{1 - X}\right)^2$$

From this law van't Hoff deduced his principle of mobile equilibrium, namely: if the reaction absorbs heat, it advances with the rise of temperature; if the reaction evolves heat, it retrogrades with rise of temperature; and if the reaction neither absorbs nor evolves heat, the state of equilibrium is stationary with rise of temperature.

Le Chatelier has extended van't Hoff's law and enunciated the important generalization: "Any change in the factors of equilibrium from outside is followed by a reversed change within the system." This rule, known as Le Chatelier's theorem, enables the chemist to foresee the influence of pressure and other agents on equilibrium. Thus, when sulfuric acid acts on sodium chloride a gas is evolved so that the system increases in volume, hence, the influence of pressure here is to retard the action.

Heat Calculations

Based on the work of Fischer,[3] Lunge [4] has calculated the heat required to convert 98 kilograms sulfuric acid and 117 kilograms sodium chloride to 142 kilograms sodium sulfate and 73 kilograms hydrochloride assuming that 30 kilograms water are volatilized with the gas; other assumptions are that the hydrogen chloride on an average has to be heated to 400° C., the steam to 500°, and the salt cake to 600°. The number of heat units required to convert 1 kilogram water at 17° into steam at 500° is taken as 812 and the specific heats of sodium sulfate and hydrochloric acid as 0.232 and 0.19 respectively:

	Heat units
Heating the Na_2SO_4 $142 \times 0.232 \times 600$	19,766
Heating the HCl $73 \times 0.19 \times 400$	5,548
Heating the H_2O 812×30	24,360
Heat consumed by the reaction	15,800
Mechanical work of gas evolution (estimated)	526
	66,000

[3] *Z. angew. Chem.*, 1888, p. 549.
[4] *Sulfuric Acid and Alkali*, Vol. 2, p. 213 (3rd Ed., 1909).

Other reactions giving hydrogen chloride:

(1) $H_2O + Cl_2 = 2HCl + O$
(in a red hot tube)
(2) $C + H_2O + Cl_2 = 2HCl + CO$
(steam)
(3) NaCl, clay and steam.
(4) NaCl, $MgCl_2$ and 10% SO_2 gas.
(5) NaCl, $MgSO_4$ and 10% SO_2 gas.
(6) NaCl, air and SO_2 gas.
(7) $CaCl_2$, sand and clay.
(8) [8] $CaCl_2 + C_2H_2 = CaC_2 + 2HCl$
(9) [8] $SiCl_4 + 2H_2O = SiO_2 + 4HCl$
(10) $CaCl_2$, iron ore and steam.
(11) $MgCl_2.6H_2O$ and heat.
(12) [7] $NH_4Cl + H_2SO_4 = NH_4HSO_4 + HCl$
$NH_4HSO_4 + NH_3 = (NH_4)_2SO_4$
(13) $2NaHSO_4 + 2NH_4Cl = (NH_4)_2SO_4 + 2HCl$
$Na_2SO_4 + (NH_4)_2SO_4 = 2NaHSO_4 + 2NH_3$
(14) $C_2H_2 + Cl_2 = C_2 + 2HCl$
(15) $3NH_4Cl + H_3PO_4 = (NH_4)_3PO_4 + 3HCl$
$(NH_4)_3PO_4 + \text{heat} = 3NH_3 + H_3PO_4$
(16) $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$
(17) [9] Salt, sand, lime and steam.

Many sulfates including sodium and potassium are changed to chlorides in the presence of excess of hydrogen chloride.

[8] Seamon, U. S. Pat. 826,614.
[8] Machalski, U. S. Pat. 745,966.
[7] Mond, U. S. Pats. 299,830; 308,511; 379,487.
[9] Walker, U. S. Pat. 474,539.

Chapter II

The Properties of Hydrochloric Acid

There is evidence that hydrochloric acid was used by men long before it was first recorded by Valentinus in the fifteenth century. Its properties have been extensively studied by the most eminent chemists, our accurate knowledge being founded on the work of Thenard, Cavendish, Gay-Lussac and Priestly.

Physical Constants of Hydrogen Chloride.[1] Hydrogen chloride has the chemical formula HCl. Its molecular weight is 36.4657 and a litre of it weighs 1.6392 gms. at 0°. Solid hydrogen chloride melts at — 111° C., and the liquid boils at — 83.1°. Hydrogen chloride has a specific gravity of 1.194 at — 85.8° and 0.748 at 33°. The critical temperature of the gas is 51.25° C. and the critical pressure is 81.6 atmospheres. Its coefficient of compressibility for pressures from 52.8 to 208.19 atmospheres is 0.00166 at 47° and 0.000397 at 57°. The liquid will dissolve less than 0.1 per cent water at 30° when it is confined at a pressure corresponding to this temperature.

Toxicity. Hydrogen chloride is a distinctly noxious gas even when greatly diluted with air although the small amount found in the air in acid plants is not injurious to men. The writer has known several hale and hearty men well past middle age who had never worked at anything else. Just as with sulfur dioxide, when the air contains enough (0.01 per cent) to injure the respiratory passages it is impossible to remain in it comfortably long enough to be affected more than temporarily. In damp weather the gas is absorbed by the moist surfaces of leaves, where it is very destructive. The law of England provides that in a cubic foot of the gas escaping from a factory into the atmosphere not more than 0.2 grain of

[1] Data from *International Critical Tables*, 1926; *Van Nostrand's Chemical Annual*, 1926, and Mellor, *Inorganic and Theoretical Chemistry*, 1922.

hydrogen chloride may be present. The distance from the plant beyond which vegetation is not affected was placed at a maximum of about 3000 yards by a Belgian Commission.

Solubility. When hydrogen chloride is generated it rapidly diffuses through the air, forming a dense fog if the air is moist. It is rapidly absorbed by water; thus, in moist weather it clings to wood and iron surfaces and penetrates paper and cloth, causing deterioration. The specific gravity of aqueous solutions of hydrochloric acid, the effect of temperature and pressure on its solubility in water, and the solubility by volume are shown in Tables 1, 2, 3, and 4, respectively.

TABLE 1.—*Specific Gravity and Per Cent by Weight of Hydrochloric Acid (Hydrogen Chloride in Aqueous Solution).*[1]

Degrees Baumé	Sp. gr.	Degrees Twaddell	Per cent HCl	Degrees Baumé	Sp. gr.	Degrees Twaddell	Per cent HCl
1.00	1.0069	1.38	1.40	11.00	1.0821	16.42	16.41
2.00	1.0140	2.80	2.82	11.25	1.0841	16.82	16.81
3.00	1.0211	4.22	4.25	11.50	1.0861	17.22	17.21
4.00	1.0284	5.68	5.69	11.75	1.0881	17.62	17.61
5.00	1.0357	7.14	7.15	12.00	1.0902	18.04	18.01
5.25	1.0375	7.50	7.52	12.25	1.0922	18.44	18.41
5.50	1.0394	7.88	7.89	12.50	1.0943	18.86	18.82
5.75	1.0413	8.26	8.26	12.75	1.0964	19.28	19.22
6.00	1.0432	8.64	8.64	13.00	1.0985	19.70	19.63
6.25	1.0450	9.00	9.02	13.25	1.1006	20.12	20.04
6.50	1.0469	9.38	9.40	13.50	1.1027	20.54	20.45
6.75	1.0488	9.76	9.78	13.75	1.1048	20.96	20.86
7.00	1.0507	10.14	10.17	14.00	1.1069	21.38	21.27
7.25	1.0526	10.52	10.55	14.25	1.1090	21.80	21.68
7.50	1.0545	10.90	10.94	14.50	1.1111	22.22	22.09
7.75	1.0564	11.28	11.32	14.75	1.1132	22.64	22.50
8.00	1.0584	11.68	11.71	15.00	1.1154	23.08	22.92
8.25	1.0603	12.06	12.09	15.25	1.1176	23.52	23.33
8.50	1.0623	12.46	12.48	15.50	1.1197	23.94	23.75
8.75	1.0642	12.84	12.87	15.75	1.1219	24.38	24.16
9.00	1.0662	13.24	13.26	16.0	1.1240	24.80	24.57
9.25	1.0681	13.62	13.65	16.1	1.1248	24.96	24.73
9.50	1.0701	14.02	14.04	16.2	1.1256	25.12	24.90
9.75	1.0721	14.42	14.43	16.3	1.1265	25.30	25.06
10.00	1.0741	14.82	14.83	16.4	1.1274	25.48	25.23
10.25	1.0761	15.22	15.22	16.5	1.1283	25.66	25.39
10.50	1.0781	15.62	15.62	16.6	1.1292	25.84	25.56
10.75	1.0801	16.02	16.01	16.7	1.1301	26.02	25.72

[1] W. C. Ferguson, for Manufacturing Chemists' Association.

Degrees Baumé	Sp. gr.	Degrees Twaddell	Per cent HCl	Degrees Baumé	Sp. gr.	Degrees Twaddell	Per cent HCl
16.8	1.1310	26.20	25.89	21.2	1.1713	34.26	33.69
16.9	1.1319	26.38	26.05	21.3	1.1722	34.44	33.88
17.0	1.1328	26.56	26.22	21.4	1.1732	34.64	34.07
17.1	1.1336	26.72	26.39	21.5	1.1741	34.82	34.26
17.2	1.1345	26.90	26.56	21.6	1.1751	35.02	34.45
17.3	1.1354	27.08	26.73	21.7	1.1760	35.20	34.64
17.4	1.1363	27.26	26.90	21.8	1.1770	35.40	34.83
17.5	1.1372	27.44	27.07	21.9	1.1779	35.58	35.02
17.6	1.1381	27.62	27.24	22.0	1.1789	35.78	35.21
17.7	1.1390	27.80	27.41	22.1	1.1798	35.96	35.40
17.8	1.1399	27.98	27.58	22.2	1.1808	36.16	35.59
17.9	1.1408	28.16	27.75	22.3	1.1817	36.34	35.78
18.0	1.1417	28.34	27.92	22.4	1.1827	36.54	35.97
18.1	1.1426	28.52	28.09	22.5	1.1836	36.72	36.16
18.2	1.1435	28.70	28.26	22.6	1.1846	36.92	36.35
18.3	1.1444	28.88	28.44	22.7	1.1856	37.12	36.54
18.4	1.1453	29.06	28.61	22.8	1.1866	37.32	36.73
18.5	1.1462	29.24	28.78	22.9	1.1875	37.50	36.93
18.6	1.1471	29.42	28.95	23.0	1.1885	37.70	37.14
18.7	1.1480	29.60	29.13	23.1	1.1895	37.90	37.36
18.8	1.1489	29.78	29.30	23.2	1.1904	38.08	37.58
18.9	1.1498	29.96	29.48	23.3	1.1914	38.28	37.80
19.0	1.1508	30.16	29.65	23.4	1.1924	38.48	38.03
19.1	1.1517	30.34	29.83	23.5	1.1934	38.68	38.26
19.2	1.1526	30.52	30.00	23.6	1.1944	38.88	38.49
19.3	1.1535	30.70	30.18	23.7	1.1953	39.06	38.72
19.4	1.1544	30.88	30.35	23.8	1.1963	39.26	38.95
19.5	1.1554	31.08	30.53	23.9	1.1973	39.46	39.18
19.6	1.1563	31.26	30.71	24.0	1.1983	39.66	39.41
19.7	1.1572	31.44	30.90	24.1	1.1993	39.86	39.64
19.8	1.1581	31.62	31.08	24.2	1.2003	40.06	39.86
19.9	1.1590	31.80	31.27	24.3	1.2013	40.26	40.09
20.0	1.1600	32.00	31.45	24.4	1.2023	40.46	40.32
20.1	1.1609	32.18	31.64	24.5	1.2033	40.66	40.55
20.2	1.1619	32.38	31.82	24.6	1.2043	40.86	40.78
20.3	1.1628	32.56	32.01	24.7	1.2053	41.06	41.01
20.4	1.1637	32.74	32.19	24.8	1.2063	41.26	41.24
20.5	1.1647	32.94	32.38	24.9	1.2073	41.46	41.48
20.6	1.1656	33.12	32.56	25.0	1.2083	41.66	41.72
20.7	1.1666	33.32	32.75	25.1	1.2093	41.86	41.99
20.8	1.1675	33.50	32.93	25.2	1.2103	42.06	42.30
20.9	1.1684	33.68	33.12	25.3	1.2114	42.28	42.64
21.0	1.1694	33.88	33.31	25.4	1.2124	42.48	43.01
21.1	1.1703	34.06	33.50	25.5	1.2134	42.68	43.40

TABLE 2.—*Effect of Temperature on the Solubility of Hydrogen Chloride in Water.*[1]

Temperature °C	HCl Per cent	Temperature °C	HCl Per cent
50	61.65	10	65.18
45	61.76	5	65.48
40	62.27	0	65.85
35	62.90	— 5	66.44
30	63.21	— 10	66.71
20	64.19	— 50	67.29
15	64.70	— 20	67.65

[1] Rupert, *J. Am. Chem. Soc.* **31**: 860.

TABLE 3.—*Effect of Pressure on the Solubility of Hydrogen Chloride in Water.*[1]

Partial pressure mm.Hg.[2]	Grams HCl per gram H_2O at °C	Partial pressure mm.Hg.[2]	Grams HCl per gram H_2O at °C	Partial pressure mm.Hg.[2]	Grams HCl per gram H_2O at °C	Partial pressure mm.Hg.[2]	Grams HCl per gram H_2O at °C
60	0.613	140	0.681	350	0.751	750	0.824
70	.628	150	.686	400	.763	800	.831
80	.640	175	.697	450	.772	900	.844
90	.649	200	.707	500	.782	1000	.856
100	.657	225	.716	550	.791	1100	.869
110	.664	250	.724	600	.800	1200	.882
120	.670	275	.732	650	.808	1300	.895
130	.676	300	.738	700	.817		

[1] Roscoe and Dittmar, *J. Chem. Soc.* **12**, 128 (1860).
[2] Total pressure minus the aqueous vapor tension.

TABLE 4.—*Solubility of Hydrogen Chloride in Water at 760 mm. Pressure and Temperatures from 0° to 23° C.*[1]

Temperature °C	Volumes HCl dissolved in one volume H_2O	Specific gravity of solution	HCl—per cent by weight
0	525.2	1.2257	46.148
4	494.7	1.2265	44.361
8	480.3	1.2185	43.828
12	471.3	1.2148	43.277
14	462.4	1.2074	42.829
18	451.2	1.2064	42.344
18.25	450.7	1.2056	42.283
23	435.0	1.2014	41.536

[1] Deike, *Pogg. Ann.* **119**, 156.

Hydrogen chloride dissolves easily in dilute aqueous solutions of other acids, for example, acetic, nitric and sulfuric; at 17° C. a solution containing 89.0 per cent sulfuric acid (H_2SO_4) will dissolve only 0.068 per cent hydrogen chloride, while anhydrous sulfuric acid does not dissolve any at all. It is easily soluble in several common organic solvents.[2] Methanol at 18° C. dissolves 46.9 per cent; ethyl alcohol at 19.2°, 41 per cent; ether at 20°, 24.9 per cent; turpentine dissolves 50 per cent but phenol dissolves very little. Glycerine, glacial acetic acid, benzene, xylene and hexane are solvents for it as well as aniline, pyridine, nitrobenzene, ketones and esters.

Solvent Action. Hydrogen chloride is one of the strongest acids, but if moisture is excluded, it does not even redden litmus paper or decompose carbonates or sulfides. Anhydrous hydrogen chloride exerts but little action on metals except aluminum. Arsenic, antimony, cadmium, silver and platinum are not attacked; lead, magnesium and tin are very slowly attacked; iron, copper and thallium only superficially.

The water solution, however, dissolves all metals except silver, mercury, arsenic, antimony, bismuth, gold and platinum. It dissolves all the sulfides, oxides and hydroxides of the metals, and decomposes the insoluble oxalates, carbonates, hypophosphites, phosphates, hydrides and sulfites.

The resistance of alloys to hydrochloric acid is shown in Table 5.

Boiling Point. Hydrogen chloride forms with water a constant boiling mixture which contains 20.24 per cent of hydrogen chloride and boils at 110° C. at 760 mm. pressure. If a weaker acid than this is distilled, water comes over in excess and the residue eventually attains the above composition and boiling point. If a stronger acid is distilled, the distillate contains excess of hydrogen chloride, while the residue grows weaker and the boiling point rises until the values for the constant boiling mixture are attained.

Roscoe and Dittmar[3] found that if the pressure is higher or lower than 760 mm. the acid distils at a concentration which varies with the pressure (see Table 6). Bonner and Branting[4] have

[2] Mellor, *Inorganic and Theoretical Chemistry*, 1922.
[3] *J. Chem. Soc.* **12**, 136 (1860).
[4] *J. Am. Chem. Soc.* **48**, 3093 (1926).

Manufacturer	Designation of Material	Material	C	Si	Mn	Ni	Cr	Fe	Cu	Zn	Sn	Al	Very Dilute	Moderate Dilution	Concentrated
Allegheny Steel Co....	Ascoloy	Wrought					14.0	*a*					Poor	Poor	Poor
Carpenter Steel Co....	Stainless	Wrought	.30				14.0	*a*					Poor	Poor	Poor
	Rustless	Wrought	.30				20.0	*a*	1.0				Poor	Poor	Poor
Crucible Steel Co.....	No. 2600 Metal	Wrought											.....	.....	Poor
Cyclops Steel Co.....	No. 17 Metal	Wrought	.45	1.00	.75	20.0	7.5	*a*					Fair	Fair	.....
Firth-Sterling Steel Co.	Stainless Steel	Wrought	.30				13.0	*a*					Poor	Poor	Poor
Ludlum Steel Co.....	Delhi Tough	Wrought	.07	1.25			17.0	*a*					Poor	Poor	Poor
	Delhi Hard	Wrought	1.20	1.50			17.0	*a*					.....	Good	Poor
	Silcrome	Wrought	.40	3.50			8.25	*a*					Poor	Poor	Poor
Midvale Steel Co.....	Stainless Low Carbon	Wrought	.35	.35	.50		15.0	*a*					Good	Good	Poor
	" Medium Carbon	Wrought	.80	.75	.50		18.0	*a*					Good	Good	Poor
	" High Carbon	.....	1.00	.35	.50		23.0	*a*					Good	Good	Poor
Driver-Harris Co.	Nichrome	Wrought				60.0	12.0	*a*					Fair	Fair	Poor
	Cimet	Cast				25.0		*a*					Poor	Poor	Poor
	Chrome Iron	Wrought and Cast					20.0	*a*					Poor	Poor	Poor
Haynes Stellite Co. ...	Stellite	Cast					*b*						.....	Poor	Poor
The Duriron Co.	Duriron	Cast	.60	14.3	.35			84.6		(P 0.16—S 0.04)			*c*	*c*	*c*
Bethlehem Fdry. & Mach. Co.	Corrosiron	Cast		13.5				85.5					Fair	Good	Fair
	Karma	Wrought				80.0	20.0						Good	Good	Fair
Electric Alloy Co.	Elalco Rayo	Wrought				85.0	15.0						Good	Good	Fair
	Elalco Calido	Wrought				60.0	16.0	*a*					Good	Good	Fair
	Elalco Comet	Wrought				30.0	5.0	*a*					Fair	Fair	Fair
	Pure Nickel	Wrought				98+							Good	Good	Fair
	Manganese Nickel	Wrought			2.0	97.0							Good	Good	Fair
	Elalco Magno	Wrought			5.0	95.0							Good	Good	Fair
Hoskins Mfg. Co.	Chromel A	Wrought				80.0	20.0						.....	*d*	*e*
International Nickel Co	Commercial Nickel	Wrought and Cast			.25	97.0							*f*	*f*	*f*
American Metal Products Co.	Ampco	Wrought and Cast					.8	82.0					Good	Good	0.489
Aterite Co., Inc.	Aterite	Wrought				10.0		2.0	65.0	23.0			Good	Good	Good
	Aterite	Cast				35.0		5.0	55.0	5.0			Not recommended		.....
Chapman Valve Mfg. Co.	Davis Metal	Cast	C+Si	0.5	1.5	29.0		2.0	67.0				.....	*g*	.....
Chase Metal Works ...	Naval Brass	Wrought							61.0	38.0	1.0		Fair	Fair	Poor
	Admiralty Tubing	Wrought							70.0	29.0	1.0		Fair	Poor	.....
	Commercial Bronze Rod	Wrought			PbO-	.75			86.0	12.8	5.0		Good	.....	Fair
	18% Nickel-Silver	Wrought				18.0			66.0	16.0			Good	Fair	.....
DuPont Engineering Co.	Everdur 50	Wrought and Cast		4.5	1.0				94.5				.....	*h*	*h*
Frontier Bronze Corp..	Titanium-Aluminum Bronze No. 1	Cast							90.0			10.0	Good	Good	Good
	Titanium-Aluminum Bronze No. 5	Cast						1.0	89.0			10.0	Good	Good	Good
Standard Calorimeter Co.	Illium	Cast		.5	1.5	63.0	21.0		8.0	Mo-4.0	Wo-2.0		.....	.....	.....

[1] Chem. & Met. Eng., **31**, 79 (1924).

a Balance, including accidental impurities.

b Series of Co-Cr-W alloys.

c Losses at room temperature in inches thickness per month × 10^5:
0.5% HCl — 12.0; 20% — 667; concentrated — 1822.
Losses at 90° C. in inches thickness per month × 10^2:
0.5% HCl — 140; 20% — 2800; concentrated — 10,170.

d Penetration in inches per month × 10^2 (room temperature): 0.05 to 0.30.

e Penetration in inches per month × 10^2 (room temperature): 5.0 to 6.0.

f Losses at room temperature in inches thickness per month × 10^2:
0.3% HCl — 0.037; 20% — 0.08; concentrated — 0.82 to 0.94.

g Penetration in inches per month × 10^2 in solutions 140° — 150° F.:
10% HCl — 0.91.

h Penetration per month at 25°. C. unagitated:
20% HCl — 0.023; concentrated 0.224.

i Loss in milligrams per square inch per month,
at 20° — 30° C.: 5% HCl — 32.9; 25% — 244.
at 70° — 75° C.: 5% HCl — 851; 10% — 1071.

TABLE 6.—*Change in strength of constant boiling acid according to pressure.*[1]

Pressure mm. Hg	HCl per cent	Pressure mm. Hg	HCl per cent	Pressure mm. Hg	HCl per cent
50	23.2	800	20.2	1700	18.8
100	22.9	900	19.9	1800	18.7
200	22.3	1000	19.7	1900	18.6
300	21.8	1100	19.5	2000	18.5
400	21.4	1200	19.4	2100	18.4
500	21.1	1300	19.3	2200	18.3
600	20.7	1400	19.1	2300	18.2
700	20.4	1500	19.0	2400	18.1
760	20.24	1600	18.9	2500	18.0

[1] Roscoe and Dittmar, *J. Chem. Soc.* **12**, 128 (1860).

pointed out that the composition of these acids is not a linear function of the pressure.

Strong hydrochloric acid exposed to air at 15° C. loses hydrogen chloride until it contains 25.2 per cent. If a current of air is passed through hydrochloric acid of any strength the result is nearly the same as when it is boiled; i.e., strong acid loses hydrogen chloride and weak acid loses water until the solution contains hydrogen chloride in the proportion in which it distils over at constant strength, as shown in Table 7.

Freezing Point. Hydrochloric acid of commercial strengths does not freeze at ordinary winter temperatures. When a supersaturated solution of the acid is cooled by refrigeration the hydrogen chloride crystallizes in three hydrated forms: monohydrate, $HCl.H_2O$, melting at — 15.25° C.;[5] dihydrate, $HCl.2H_2O$, melting at 0°;[2] and trihydrate, $HCl.3H_2O$, melting at — 244°.[6] Acid containing 25 per cent hydrogen chloride must be cooled to — 80° to crystallize out the latter hydrate; the dihydrate crystallizes when a 44 per cent solution is cooled to — 26°; and the monohydrate crystallizes at — 15° from liquid hydrogen chloride with a small amount of water. Ice forms in weak solutions thus: in 10 per cent HCl at — 20°; in 15 per cent HCl at — 30°; in 20 per cent HCl at — 60°; and in 24 per cent HCl at — 80°.

[5] Rupert, *J. Am. Chem. Soc.* **31**, 851 (1909).
[6] Pickering, *Ber.* 1893, p. 279.

TABLE 7.—*Composition, at various temperatures, of hydrochloric acid through which air has been passed until strength is constant.*[1]

Temperature °C	HCl per cent	Temperature °C	HCl per cent	Temperature °C	HCl per cent
0	25.0	35	23.9	70	22.6
5	24.9	40	23.8	75	22.3
10	24.7	45	23.6	80	22.0
15	24.6	50	23.4	85	21.7
20	24.4	55	23.2	90	21.4
25	24.3	60	23.0	95	21.1
30	24.1	65	22.8	100	20.7

[1] Roscoe and Dittmar, *J. Chem. Soc.* **12**, 128 (1860).

Specific Heat.[2] Hydrochloric acid containing n mols of water per mol of hydrogen chloride has a specific heat, c, of:

n	5.20	10	20	50	100	200
c	0.660	0.749	0.855	0.932	0.964	0.970

The specific heat of the gas at constant pressure is 0.1867 and at constant volume 0.1364, both referred to water.

Compressibility.[7] Concentrated hydrochloric acid is only slightly more compressible than water.

Viscosity.[8] The viscosity of hydrochloric acid relative to water, in mols per liter, is:

N (mols per liter)	2	4	6	8	10	12
Viscosity	1.1234	1.2572	1.4108	1.6041	1.8432	2.1387

Electrolysis. When solutions of hydrochloric acid are electrolyzed hydrogen comes off at the cathode and chlorine at the anode. More or less oxygen is also formed at the anode depending on the dilution, the form of the cell, and the material of the electrodes. The arrangement of the cell [9] can be such that about half the chlorine combines with oxygen to form perchloric acid. This process is used commercially.[10]

Transport Number. For chioride ions in 0.002 N solution of hydrogen chloride, 0.171 at 18°; in 0.05 N solution, 0.166 at 18°; in 0.977 N solution, 0.155 at 20°.

[7] Roentgen & Schneider, *Wied. Ann.* 29, 132 (1886).
[8] Green, *J. Chem. Soc.* **93**, 2023 (1908).
[9] Goodwin & Walker, *Chem. & Met. Eng.* **25**, 1093.
[10] U. S. Pat. 931,944.

TABLE 8.—*Ionization of hydrogen chloride at 25° C.*[1]

Mols of HCl per liter	Per cent ionized	Mols H^+ per liter	Grams H^+ per liter	pH
2.0	69.3	1.386	1.397	−0.14
1.0	79.6	0.796	0.802	0.10
0.9	81.5	0.734	0.739	0.13
0.8	83.3	0.666	0.671	0.18
0.7	84.7	0.593	0.598	0.23
0.6	86.5	0.519	0.523	0.28
0.5	87.5	0.438	0.441	0.36
0.4	88.7	0.355	0.358	0.45
0.3	90.1	0.270	0.272	0.57
0.2	92.0	0.184	0.186	0.74
0.10	94.8	0.095	0.096	1.02
0.09	95.2	0.086	0.086	1.07
0.08	95.6	0.076	0.077	1.12
0.07	95.8	0.067	0.068	1.17
0.06	96.4	0.058	0.058	1.24
0.05	96.8	0.048	0.049	1.32
0.04	97.6	0.039	0.039	1.41
0.03	98.0	0.029	0.030	1.54
0.02	98.8	0.020	0.020	1.7
0.010	99.8	0.0100	0.0101	2.00
0.009	99.9	0.0090	0.0091	2.05
0.008	100.0	0.0080	0.0081	2.10
0.007	100.0	0.0070	0.0071	2.15
0.006	100.0	0.0060	0.0060	2.22
0.005	100.0	0.0050	0.0050	2.30
0.004	100.0	0.0040	0.0040	2.40
0.003	100.0	0.0030	0.0030	2.52
0.002	100.0	0.0020	0.0020	2.7
0.001	100.0	0.0010	0.0010	3.0

[1] Van Nostrand's Chemical Annual, 1926.

Electrical Conductivity. The molecular conductivity of hydrochloric acid at 18° C.[2] and at 25° [11] is as follows:

At 18° C.						
N	0.5	1	3	5	7	10
Λ	327	301	215	152.2	106.2	64.4
At 25° C.						
N	0.1	0.5	1.0	2.0	3.0	4.0
Λ	391.33	361.31	333.52	285.10	240.40	210.60

Rate of Diffusion.[12] The diffusion coefficient for hydrochloric acid gas is 490×10^{-7} square centimeters per second. The diffusion

[11] Ruby & Kawai, *J. Am. Chem. Soc.* **48**, 1119 (1926).
[12] Sheffer, *Ber.* **15**, 788 (1882).

coefficient of hydrogen chloride in water in square centimeters per day is:

N	4.23	3.28	2.43	1.775	0.962	0.210
Coefficient 0° C.....	2.31	2.08	1.86	1.67	1.52	1.39
Coefficient 19.2°		3.89				

Coefficient of Thermal Expansion.[13] Hydrochloric acid of specific gravity 1.000 to 1.040 increases or decreases in gravity 0.002 per degree below or above the standard 15° C.; acid between 1.041 and 1.085—0.003 per degree; 1.086 to 1.120—0.004 per degree; 1.121 to 1.155—0.005 per degree; and 1.156 to 1.200—0.006 per degree.

Heat of Solution.[14] The heat generated by the absorption of a mol of hydrogen chloride in *N* mols of water:

N	1	2	5	10	50	100	200
calories	5.375	11.365	14.959	16.157	17.115	17.235	17.315

Heat of Neutralization.[2] With equivalent amounts of the hydroxides of sodium, potassium, ammonium, calcium, barium and magnesium the heat of neutralization is between 12 and 14 calories; for the oxides of mercury, zinc, cadmium, manganese, iron, cobalt and nickel, between 9 and 11 calories.

Free Energy. Bates and Kirschman[15] have reported the free energy of hydrogen chloride in solutions of various concentrations at 25° C.:

N	0.1	6.0	7.0	8.0	9.0	10.0
calories	—34,330	—27,790	—27,250	—26,725	—26,225	—25,775

Vapor Pressure. The vapor pressure of hydrogen chloride at various temperatures has been investigated by Faraday,[16] who reported as follows:

Temperature, °C....	—73.33	—45.56	—17.78	—0	—18.1	33.4	50.56
Pressure, in atmospheres	1.80	6.30	15.04	26.20	41.8	58.85	85.33

[13] Lunge & Marchlewsky, *Zeit. angew. Chem.* **4**, 133 (1891).
[14] Thomsen, *Thermochemische Untersuchungen*, Leipsig, 1882.
[15] *J. Am. Chem. Soc.* **41**, 1991 (1919).
[16] *Phil. Trans.* **135**, 155 (1845).

Zeisberg [17] has developed a formula for the partial pressure of hydrogen chloride in aqueous solutions with an error of less than 5 per cent in the range from 18 to 32 per cent HCl at temperatures from 0° to 100° C.:

$$\log. P = 10.9528 - 0.009725\,W - 0.000868\,W^2 - \frac{4.557 - 65.3\,W}{T}$$

Where P = pressure of hydrogen chloride in mm. mercury
W = per cent by weight of hydrogen chloride in solution
T = absolute temperature in degrees C.

The water and hydrogen chloride vapor pressures for hydrochloric acid assembled from various sources by Zeisberg are given in Tables 9 and 10.

TABLE 9.—*Water vapor pressure of hydrochloric acid solutions.*[1]

Per cent HCl in soln.	0 Deg.	Vapor Pressure in mm. Hg						
		5	10	15	20	25	30	35
6	4.18	6.04	8.45	11.7	15.9	21.8	29.1	39.4
10	3.84	5.52	7.70	10.7	14.6	20.0	26.8	35.5
14	3.39	4.91	6.95	9.65	13.1	18.0	24.1	31.9
18	2.87	4.21	5.92	8.26	11.3	15.4	20.6	27.5
20	2.62	3.83	5.40	7.50	10.3	14.1	19.0	25.1
22	2.33	3.40	4.82	6.75	9.30	12.6	17.1	22.8
24	2.05	3.04	4.31	6.03	8.30	11.4	15.4	20.4
26	1.76	2.60	3.71	5.21	7.21	9.95	13.5	18.0
28	1.50	2.24	3.21	4.54	6.32	8.75	11.8	15.8
30	1.26	1.90	2.73	3.88	5.41	7.52	10.2	13.7
32	1.04	1.57	2.27	3.25	4.55	6.37	8.70	11.7
34	0.85	1.29	1.87	2.70	3.81	5.35	7.32	9.95
36	0.68	1.03	1.50	2.19	3.10	4.41	6.08	8.33
38	0.53	0.81	1.20	1.75	2.51	3.60	5.03	6.92
40	0.41	0.63	0.94	1.37	2.00	2.88	4.09	5.68
42	0.31	0.48	0.72	1.06	1.56	2.30	3.28	4.60

Per cent HCl in soln.	Vapor Pressure in mm. Hg								
	40	45	50	60	70	80	90	100	110
6	50.6	66.2	86.0	139	220	333	492	715	...
10	47.0	61.5	80.0	130	204	310	463	677	960
14	42.1	55.3	72.0	116	185	273	425	625	892
18	36.4	47.9	62.5	102	162	248	374	550	783
20	33.3	43.6	57.0	93.5	150	230	345	510	729
22	30.2	39.8	52.0	85.6	138	211	317	467	670
24	27.1	35.7	46.7	77.0	124	194	290	426	611
26	24.0	31.7	41.5	69.0	112	173	261	388	554
28	21.1	27.9	36.5	60.7	99.0	154	234	349	499
30	18.4	24.3	32.0	53.5	87.5	136	207	310	444
32	15.7	21.0	27.7	46.5	76.5	120	184	275	396
34	13.5	18.1	24.0	40.5	66.5	104	161	243	355
36	11.4	15.4	20.4	34.8	57.0	90.0	140	212	311
38	9.52	13.0	17.4	29.6	49.1	77.5	120	182	266
40	7.85	10.7	14.5	25.0	42.1	67.3	105	158	230
42	6.45	8.90	12.1	21.2	35.8	57.2	89.2	135	195

[1] Zeisberg, *Chem. & Met. Eng.* **32** 326 (1925).

[17] *Chem. & Met. Eng.* **32**, 326 (1925).

TABLE 10.—*Partial pressure of hydrogen chloride over its aqueous solutions.*

Per cent HCl	0 Deg.	Vapor Pressure in mm. Hg						
		5	10	15	20	25	30	35
2	.....	.....	0.0000117	0.000023	0.000044	0.000084	0.000151	0.000275
4	0.000018	0.000036	0.000069	0.000131	0.00024	0.00044	0.00077	0.00134
6	0.000066	0.000125	0.000234	0.000425	0.00076	0.00131	0.00225	0.0038
8	0.000118	0.000323	0.000583	0.00104	0.00178	0.0031	0.00515	0.0085
10	0.00042	0.00075	0.00134	0.00232	0.00395	0.0067	0.0111	0.0178
12	0.00099	0.00175	0.00305	0.0052	0.0088	0.0145	0.0234	0.037
14	0.0024	0.00415	0.0071	0.0118	0.0196	0.0316	0.050	0.078
16	0.0056	0.0095	0.016	0.0265	0.0428	0.0685	0.106	0.163
18	0.0135	0.225	0.037	0.060	0.095	0.148	0.228	0.345
20	0.0316	0.052	0.084	0.132	0.205	0.32	0.48	0.72
22	0.0734	0.119	0.187	0.294	0.45	0.68	1.02	1.50
24	0.175	0.277	0.43	0.66	1.00	1.49	2.17	3.14
26	0.41	0.64	0.98	1.47	2.17	3.20	4.56	6.50
28	1.0	1.52	2.27	3.36	4.90	7.05	9.90	13.8
30	2.4	3.57	5.23	7.60	10.6	15.1	21.0	28.6
32	5.7	8.3	11.8	16.8	23.5	32.5	44.5	60.0
34	13.1	18.8	26.4	36.8	50.5	68.5	92	122
36	29.0	41.0	56.4	78	105.5	142	188	246
38	63.0	87.0	117	158	210	277	360	465
40	130	176	233	307	399	515	627	830
42	253	332	430	560	709	900	.....	.....
44	510	655	840	.....	.....	.....	.....	.....
46	940	.....	.....	.....	.....	.....	.....	.....

Per cent HCl	Vapor Pressure in mm. Hg								
	40	45	50	60	70	80	90	100	110
2	0.00047	0.00083	0.00140	0.00380	0.0100	0.0245	0.058	0.132	0.280
4	0.0023	0.00385	0.0064	0.0165	0.0405	0.095	0.21	0.46	0.93
6	0.0062	0.0102	0.0163	0.040	0.094	0.206	0.44	0.92	1.78
8	0.0138	0.022	0.0344	0.081	0.183	0.39	0.82	1.64	3.10
10	0.0282	0.045	0.069	0.157	0.35	0.73	1.48	2.9	5.4
12	0.058	0.091	0.136	0.305	0.66	1.34	2.65	5.1	9.3
14	0.121	0.185	0.275	0.60	1.25	2.50	4.8	9.0	16.0
16	0.247	0.375	0.55	1.17	2.40	4.66	8.8	16.1	28
18	0.515	0.77	1.11	2.3	4.55	8.6	15.7	28	48
20	1.06	1.55	2.21	4.4	8.5	15.6	28.1	49	83
22	2.18	3.14	4.42	8.6	16.3	29.3	52	90	146
24	4.5	6.4	8.9	16.9	31.0	54.5	94	157	253
26	9.2	12.7	17.5	32.5	58.5	100	169	276	436
28	19.1	26.4	35.7	64	112	188	309	493	760
30	39.4	53	71	124	208	340	542	845	.....
32	81	107	141	238	390	623	970	.....	.....
34	161	211	273	450	720	.....	.....	.....	.....
36	322	416	535	860	.....	.....	.....	.....	.....
38	598	758	955	.....	.....	.....	.....	.....	.....
40	.....	.....	.....	.....	.....	.....	.....	.....	.....
42	.....	.....	.....	.....	.....	.....	.....	.....	.....
44	.....	.....	.....	.....	.....	.....	.....	.....	.....
46	.....	.....	.....	.....	.....	.....	.....	.....	.....

Principal uses for hydrochloric acid:

Cleaning steel wire and plate before galvanizing.
Glue making.
Zinc chloride manufacture.
Cleaning steel plate before tinning.
Manufacture of organic chemical: aniline, diphenylamine, etc.
Preparation of activated carbon.

Recovery of zinc from galvanized scrap.
Manufacture of organic salts: ammonium chloride, barium chloride, magnesium chloride, etc.
Hydrolyzing starch in making glucose.
Hydrolyzing wood in making alcohol.
Manufacture of raw sugar.
Sugar refining.
Saponifying animal and vegetable oils and fats.
Hydrometallurgy of platinum, gold, silver, cobalt and other metals.
Electroplating.
In leather tanning and dyeing.
As a sour in bleaching.
Making blanc fixe.
Carbonizing wool.
Cleaning stone work.
Various uses in dyeing fabrics.
Preparing artificial human hair.

TABLE 11.—*Production of hydrochloric acid in the United States, 1923 and 1925.*[1]

	1923	1925
Hydrochloric acid:		
Number of establishments	39	37
Total production, tons	218,521	225,369
For sale, tons	155,814	152,587
Value	$3,102,172	$2,941,175
Average per ton	$ 20	$ 19
Production according to strength, tons:		
18° Baumé	32,442	25,362
20° Baumé	181,131	198,761
22° Baumé	3,098	
24° Baumé (100 per cent)	1,145	1,246
C. P.	705	
Total production basis 100 per cent, tons	69,092	
Production by states, tons:		
New Jersey (5 plants)	22,936	
Pennsylvania (5 plants)	18,234	
New York (6 plants)	16,660	
California (4 plants)	6,536	
Ohio (3 plants)	38,161	
Illinois (3); Connecticut (2); Mass. (2); Michigan (2). Ark., Colo., Del., Kans. Ind., La., W. Va. (1 each)	115,994	

[1] Department of Commerce, Census of Manufactures.

Chapter III

Sodium Sulfate—Properties, Occurrence, Production and Consumption

Sodium sulfate occurs in nature mixed with other salts in almost all waters and in various minerals. The principal forms of sodium sulfate in commerce, however, are manufactured, and include a coarse white powder containing 92 to 96 per cent sodium sulfate (Na_2SO_4); Glauber's salt, pure colorless, crystalline sodium sulfate ($Na_2SO_4.10H_2O$); and pure anhydrous Glauber's salt.

Physical Constants. The molecular weight of sodium sulfate is 142.059; it melts at 843° C. and partly volatilizes at 1400°; its heat of solution at 100° is 780 calories and the heat formation of Na_2,S,O_4 = 328,600 calories; its specific heat is 0.232.

Solubility. Reference to Tables 12 and 13 shows that the solubility of sodium sulfate in water increases from 0° to 32.28° C., then gradually decreases to 103.5°, which is the boiling point of the saturated solution. Under 18° anhydrous sodium sulfate cannot exist in the presence of water but is converted into the heptahydrate ($Na_2SO_4.7H_2O$) or the decahydrate ($Na_2SO_4.10H_2O$). The solubility of the heptahydrate increases with the temperature from 0 to 26°, and at 27° it is converted into the anhydrous salt. Thus there are two different rates of solubility for sodium sulfate from 0 to 18°, three from 18 to 26°, two from 26 to 34°, and only one above 34°.

The change which takes place in a saturated solution at 32.38° C. consists in the conversion of the decahydrate to the anhydrous salt. It is a chemical change taking place with the absorption of heat and the solubility curve shows a sharp break at that temperature which is called the transition point. This transition temperature is lowered by the presence of other salts thus, with aphthitalite

TABLE 12.—*Solubility of sodium sulfate in 100 parts water at 0°-103° C.*[1]

Temperature (°C.)	Parts Na_2SO_4	Temperature (° C.)	Parts Na_2SO_4	Temperature (° C.)	Parts Na_2SO_4
0	4.8	35	50.2	70	44.4
1	5.1	36	49.9	71	44.3
2	5.4	37	49.6	72	44.2
3	5.7	38	49.3	73	44.2
4	6.0	39	49.1	74	44.1
5	6.4	40	48.8	75	44.0
6	6.8	41	48.5	76	44.0
7	7.3	42	48.3	77	43.9
8	7.8	43	48.1	78	43.8
9	8.4	44	47.9	79	43.7
10	9.0	45	47.7	80	43.7
11	9.7	46	47.5	81	43.6
12	10.5	47	47.3	82	43.5
13	11.4	48	47.1	83	43.5
14	12.4	49	46.9	84	43.4
15	13.4	50	46.7	85	43.3
16	14.5	51	46.6	86	43.3
17	15.7	52	46.4	87	43.2
18	16.9	53	46.2	88	43.2
19	18.2	54	46.1	89	43.1
20	19.5	55	45.9	90	43.1
21	20.9	56	45.8	91	43.0
22	22.5	57	45.7	92	43.0
23	24.1	58	45.6	93	42.9
24	25.9	59	45.4	94	42.9
25	27.9	60	45.3	95	42.8
26	30.1	61	45.2	96	42.7
27	32.4	62	45.1	97	42.6
28	35.0	63	45.0	98	42.6
29	37.8	64	44.9	99	42.5
30	40.9	65	44.8	100	42.5
31	44.2	66	44.7	101	42.4
32	47.8	67	44.6	102	42.3
32.75	50.65	68	44.5	103	42.2
33	50.6	69	44.5	103.5	42.2
34	50.4	...	...	...	...

[1] Mulder, *Scheik. Verhandel.* 1864, p. 123.

($[Na,K]_2SO_4$) it is 30.1°; with sodium chloride, 17.9°; and with sodium chloride and aphthitalite only 16.3°.

Supersaturated solutions of sodium sulfate are easily formed; when sodium sulfate solution saturated at its boiling point is hermetically sealed no crystals are deposited on cooling; the same is true if the flask is closed by cotton wool and often by merely

TABLE 13.—*Solubility of sodium sulphate in water.*

Temperature (°C.)	Solid phase	Grams anhydrous Na_2SO_4 to 100 grams H_2O	Authority
—1.2	Ice and Glauber's salt ...	4.0	De Coppet, *Zeitschr. physikal. Chemie*, vol. 22, p. 239, 1897.
—3.55	Ice and $Na_2SO_4.7H_2O$ ..	14.5	
0	Glauber's salt	5.0	Loewel, *Annales chimie et phys.*, 3d ser., vol. 49, p. 50, 1857.
10	.... do	9.0	
15	.... do	13.2	
20	.... do	19.4	
25	.... do	28.0	
30	.... do	40.0	
0	$Na_2SO_4.7H_2O$	19.6	
10	.... do	30.5	
20	.... do	44.7	
26	.... do	55.0	
18	Na_2SO_4	53.3	
20	.... do	52.8	
24.4	$Na_2SO_4.7H_2O$ & Na_2SO_4	51.8	
25	.... do	51.5	
30	.... do	50.4	
32.383	Glauber's salt & Na_2SO_4.	...	Richards and Wells, *Zeitschr. physikal. Chemie*, vol. 43, p. 465, 1903.
35	Na_2SO_4	49.4	Gay-Lussac, *Annales chimie et phys.*, vol. 11, p. 312, 1819.
40	.... do	48.2	
50	.... do	46.8	
60	.... do	45.5	
70	.... do	44.5	
80	.... do	43.7	
90	.... do	42.9	
100	.... do	42.7	

covering it in a beaker with a watch glass or card or putting a layer of oil on the solution. Addition of a crystal of Glauber's salt causes crystallization.

A hot solution containing equal parts of water and the monohydrate will not crystallize on cooling if kept in a closed vessel or otherwise protected, but crystallization may be brought about instantaneously by exposing to the air and agitating.

The solubility of sodium sulfate varies slightly with the pressure, thus: a solution saturated at 0° C. contains 4.40 parts Na_2SO_4 per 100 at 1 atmosphere and 4.53 parts at 20 atmospheres; and a solu-

tion saturated at 15° contains 11.32 parts at 1 atmosphere and 10.33 parts at 40 atmospheres. It dissolves in solutions of ammonium chloride, ammonium nitrate, potassium nitrate, sodium nitrate, the sulfates of potassium, magnesium, copper, etc., and also in some organic solvents such as alcohol and glycerine, but not in acetone or methyl and ethyl acetates. Added to a solution of potassium chloride it throws out potassium sulfate.

Sodium sulfate dissolves in sulfuric acid, from which solution it can be crystallized as Glauber's salt. (*See* Table 14.)

TABLE 14.—*Solubility of sodium sulfate in dilute sulfuric acid at 25° C.*[1]

Mol. per 1000 g. of solution		Solid phase
Na_2SO_4	H_2SO_4	
1.55	0.08	Na_2SO_4
1.59	0.147	"
1.85	0.60	Na_2SO_4, $10H_2O$
2.00	0.763	"
0.77	4.23	$NaHSO_4$, H_2O
0.47	4.96	"
0.32	6.61	Na_2HSO_4
0.305	6.87	"
0.07	7.18	$Na_2H(SO_4)_2$
0.79	8.78	"

[1] D'ans, *Z. anorg. Chem.* **61**, 92 (1909).

Electrolysis. Sodium sulfate can be electrolyzed in ordinary chlorine cells to produce caustic soda and dilute sulfuric acid. Atwell and Fuwa [1] state that the production cost of caustic soda made by electrolysis of sodium sulfate solution compares favorably with that from sodium chloride and there is saving in the cost of raw materials when waste solutions of sodium sulfate are used for the production of caustic and sulfuric acid for local consumption.

Natural Sodium Sulfate

The United States Geological Survey has published a bulletin (No. 717) which fully covers the various features of the production of salt cake and Glauber's salt from natural deposits in the United States up to 1923, the date of its publication. Over fifty

[1] *Ind. Eng. Chem.* **15**, 617 (1923).

locations of sodium sulfate are mentioned, many being described quite thoroughly. They consist in some cases of lake and spring waters, but the large majority are layers or crusts or heavily impregnated sands. All of the noteworthy deposits occur in the Western States. Every Rocky Mountain State excepting Montana appears to possess workable locations whenever the demand warrants the undertaking.

Sodium sulfate occurs unmixed in two mineral forms, thenardite [2] and mirabilite.[3] In many instances it is associated with other soluble salts in mineralized form. These minerals are principally: aphthitalite, a double sulfate of sodium and potassium, $(Na,K)_2SO_4$; bloedite, hydrated double sulfate of sodium and magnesium, $Na_2SO_4.MgSO_4.4H_2O$; glauberite, anhydrous sodium-calcium sulfate, $Na_2SO_4.CaSO_4$; and hanksite, a triple salt, $9Na_2SO_4.2Na_2CO_3.KCl$.

Most of the deposits contain the double salt minerals and where sodium sulfate alone is the soluble constituent, as in the crusts mentioned, it is shown to be the result of fractional crystallization. This is the method that would be required to work some of the largest deposits and it is said to be unprofitable at present prices,

[2] *Thenardite*—Anhydrous sodium sulfate, Na_2SO_4. Composition, sodium oxide (Na_2O), 56.3 per cent; sulfur trioxide (SO_3), 43.7 per cent. Crystal orthorhombic : axial ratio, $a : b : c = 0.5976 : 1 : 1.2524$; (100) $\wedge$ (100) = 30° 52′, (001) $\wedge$ (101) = 64° 30′, (001) $\wedge$ (011) = 51° 24′; common forms, *c* (001), *a* (110), *m* (110), *o* (111), *t* (106). Twinning planes (101) and (011); habit, in pyramidal and tabular crystals, commonly in crossed twins. Cleavage, basal distinct. Hardness, 2.5. Specific gravity, 2.698. Color, white, gray, or brownish. Transparent to translucent. Indices of refraction: α 1.464; β 1.474; γ 1.485. Optically positive. Axial plane parallel to (001); acute bisectrix normal to *b* (010). Axial angle nearly 90, $\rho > V$ perceptible. Very soluble in water. Taste faintly saline.

[3] *Mirabilite*—Hydrated sodium sulfate, $Na_2SO_4.10H_2O$. Composition, sodium sulfate (Na_2SO_4), 44.1 per cent; water (H_2O), 55.9 per cent. Crystals monoclinic: axial ratio, $a : b : c$ 1.1158 : 1 : 1.2372; β = 72° 15′ = (001) $\wedge$ (100), (100) $\wedge$ (110) = 46° 44′, (001) $\wedge$ = 55° 55′, (001) $\wedge$ (011) = 49° 41′; common forms, *a* (100), *b* (010), *c* (001), *m* (110), *r* (101); habit, long prismatic, almost needle-like, elongated parallel to *b* axis, also short, stout prismatic, elongated parallel to vertical axis *c* (somewhat resembling borax). Cleavage, *a* perfect. Hardness, 1.5-2. Specific gravity, 1.48. Colorless, transparent to white opaque. Luster vitreous. Indices of refraction: α = 1.394; β = 1.396; γ = 1.398. Optically negative. Axial plane and acute bisectrix normal to *b* (010). Axial angle very large, cross dispersion very strong, no extinction in white light. Taste slightly bitter. Very readily soluble in water.

except where potassium salts are sufficiently abundant to be recovered as the primary product.

A valuable study of solubilities with mixtures of the salts which occur in the natural states is contained in the aforementioned Geological Survey Bulletin, which concludes that the best way to separate sodium sulfate from certain mixtures is to chill the solutions and produce Glauber's salt. Table 15 gives the analyses of

TABLE 15.—*Composition of solutions saturated with certain salts.*[1]
(In grams per 100 grams of water.)

Temperature (°C.)	Saturated with	NaCl	KCl	Na_2SO_4	K_2SO_4	Specific gravity of solution
0	Na_2SO_4	.....	.....	4.62	.....	1.043
	K_2SO_4	.....	.....	.....	7.23	1.063
	KCl	.....	28.20	.....	.....	1.153
	NaCl	34.95	.....	.....	.....	1.206
	Glauber's salt and K_2SO_4	.....	.....	6.30	9.00	1.118
	K_2SO_4 and KCl	.....	27.88	.....	1.21	.....
	NaCl and KCl	31.53	10.55	.....	.....	.....
	NaCl and Glauber's salt	34.48	.....	1.70	.....	1.185
	K_2SO_4, KCl, aphthitalite	13.38	17.78	.....	2.78	1.188
	NaCl, Glauber's salt, KCl	32.08	7.81	.....	3.62	1.240
	KCl, Glauber's salt, aphthitalite	27.07	10.06	.....	3.24	1.232
	K_2SO_4, Glauber's salt, aphthitalite	7.46	13.24	4.73	.....	.....
25	Na_2SO_4	.....	.....	27.93	.....	1.212
	K_2SO_4	.....	.....	.....	12.02	1.088
	KCl	.....	36.96	.....	.....	1.187
	NaCl	35.63	.....	.....	.....	1.199
	Na_2SO_4 and aphthitalite	.....	.....	30.97	9.31	1.282
	K_2SO_4 and aphthitalite	.....	.....	6.69	13.24	1.149
	K_2SO_4 and KCl	.....	36.63	.....	1.53	1.190
	KCl and NaCl	29.88	16.28	.....	.....	1.237
	NaCl and Na_2SO_4	32.16	.....	9.81	.....	1.239
	Na_2SO_4 and Glauber's salt	18.82	.....	21.68	.....	1.243
	Na_2SO_4, Glauber's salt, aphthitalite	14.28	.....	22.28	7.32	1.273
	KCl, K_2SO_4, aphthitalite	6.78	29.38	.....	2.23	1.200
	KCl, NaCl, aphthitalite	27.96	16.37	3.51	.....	1.250
	NaCl, Na_2SO_4, aphthitalite	34.90	.....	2.25	11.03	1.266

[1] Blasdale, *J. Ind. Eng. Chem.* 10, 344.

TABLE 15 (*Cont.*).—*Composition of solutions saturated with certain salts.*
(In grams per 100 grams of water.)

Temperature (°C.)	Saturated with	NaCl	KCl	Na_2SO_4	K_2SO_4	Specific gravity of solution
50	Na_2SO_4	.....	.....	44.84	.....	1.301
	K_2SO_4	.....	.....	.....	17.09	1.110
	KCl	.....	43.12	.....	.....	1.198
	NaCl	36.50	.....	.....	.....	1.188
	Na_2SO_4 and aphthitalite	.....	.....	45.73	9.40	1.351
	K_2SO_4 and aphthitalite	.....	.....	6.79	17.36	1.307
	KCl and K_2SO_4	.....	42.24	.....	1.84	1.212
	KCl and NaCl	29.09	22.03	.....	.....	1.246
	NaCl and Na_2SO_4	33.70	.....	7.34	.....	1.223
	K_2SO_4, KCl, aphthitalite	4.68	35.06	.....	2.59	1.203
	KCl, NaCl, aphthitalite	26.84	22.43	3.15	.....	1.254
	NaCl, Na_2SO_4, aphthitalite	40.15	14.58	11.74	.....	1.248
75	Na_2SO_4	.....	.....	43.41	.....	1.286
	K_2SO_4	.....	.....	.....	20.80	1.120
	KCl	.....	49.70	.....	.....	1.204
	NaCl	37.75	.....	.....	.....	1.183
	Na_2SO_4 and aphthitalite	.....	.....	42.06	11.77	1.332
	K_2SO_4 and aphthitalite	.....	.....	10.09	18.60	1.183
	K_2SO_4 and KCl	.....	48.75	.....	2.12	.....
	NaCl and KCl	27.87	29.06	.....	.....	1.249
	NaCl and Na_2SO_4	35.46	.....	6.67	.....	1.210
	K_2SO_4, KCl, aphthitalite	5.71	42.58	.....	2.83	1.223
	KCl, NaCl, aphthitalite	25.45	29.38	3.33	.....	1.257
	NaCl, Na_2SO_4, aphthitalite	28.28	15.72	8.88	.....	1.253
100	Na_2SO_4	.....	.....	41.68	.....	1.264
	K_2SO_4	.....	.....	.....	23.44	1.134
	KCl	.....	56.20	.....	.....	1.217
	NaCl	39.40	.....	.....	.....	1.175
	Na_2SO_4 and aphthitalite	.....	.....	41.70	13.62	1.326
	K_2SO_4 and aphthitalite	.....	.....	13.57	20.51	1.213
	K_2SO_4 and KCl	.....	54.43	.....	2.83	1.225
	NaCl and KCl	27.39	35.16	.....	.....	1.253
	NaCl and Na_2SO_4	36.56	.....	6.41	.....	1.204
	K_2SO_4, KCl, aphthitalite	3.19	50.01	.....	3.24	1.233
	KCl, NaCl, aphthitalite	24.82	36.13	43.77	.....	1.269
	NaCl, Na_2SO_4, aphthitalite	35.84	10.18	.....	11.00	1.256

solutions saturated with mixtures of various salts, as determined by W. C. Blasdale. Blasdale's original and valuable work on solutions of mixed salts is now available in book form.[4]

John E. Teeple, whose accomplishments in making the recovery of salts from Searles Lake commercially successful have won him the Perkin Medal, has in preparation a book [5] on the scientific and technical aspects of the work which will be worthy of study in relation to sodium sulfate recovery from natural deposits.

Sodium Sulfate from Lake Brines

Searles Lake and Owens Lake in California are huge stores of salts. The brine of the latter has been estimated to carry 46.6 million metric tons of sodium carbonate, 11.08 of sodium bicarbonate, 19.4 of sodium sulfate, 51.5 of sodium chloride, 5.53 of potassium chloride and 3.55 of borax. For analyses of the brines see Table 16.

Table 16.—*Soluble salts in lake brine.*

Salt	Searles Lake Per cent	Owens Lake Per cent
NaCl	16.54	9.87
KCl	4.82	1.08
Na_2CO_3	4.82	8.32
$Na_2B_4O_7$	1.50	.64
Na_2SO_4	7.16	3.77
$NaHCO_3$		1.87

It is the opinion of Chapman [6] that sodium sulfate could be obtained from Searles Lake brine at least in crude form and a market developed for the product for such uses as the manufacture of glass and paper pulp; and that a safe prediction is that processes will be developed for the commercial production of all of the salts contained in the brine of both of these lakes. There are three operating companies at Owens Lake and four at Searles Lake but none of them recovers sodium sulfate.

[4] Am. Chem. Soc. Technologic Monograph, *Equilibria in Saturated Salt Solutions.*

[5] Am. Chem. Soc. Technologic Monograph, *The Industrial Development of Searles Lake Brines, with Equilibrium Data.*

[6] *Chem. & Met. Eng.* 24, 683 (1921).

Dolbear Process. The Dolbear recovery process as reported by Bragg and Putnam [7] consists in agitating and heating the dry salt mixture from the lake, after solar evaporation, with a solution of the same mixture saturated when cold. The potassium chloride and borax being much more soluble in hot than cold solution and the solubility of the others being about the same, a separation is effected. The mixture is centrifuged hot and the hot brine allowed to cool undisturbed, when the potassium chloride crystallizes. The cool brine is then agitated and the borax separates; the brine is used over again. The leached salts containing sodium chloride, sodium sulfate and sodium carbonate are further leached with sodium chloride solution of the right concentration to dissolve the last two but not the sodium chloride. The clear solution is then treated with carbon dioxide to separate bicarbonate and then gaseous ammonia is added to the mother liquor to separate anhydrous sodium sulfate.

Operations in Nevada. The American Sodium Company has taken over the 20-year government lease originally granted to the California-Nevada Sodium Sulfate Co., on 1440 acres of saline deposit near Wabuska, Nev., one mile from the Southern Pacific lines. This lease stipulates that one-eighth of the receipts be returned to the United States Treasury.[8] A typical analysis of the material is as follows: [9]

	Per cent
Na_2SO_4	98.19
Na_2CO_3	0.13
NaCl	0.23
Insoluble and dirt	0.52
Moisture	0.23
Undetermined	0.7
Loss at 110° C	16.0

Camp Verde Valley Deposit. The Sodium Products Corporation of Prescott, Ariz., is now working a deposit at Camp Verde Valley.[10] The raw material is thenardite associated with about 10 per cent sodium chloride and other impurities. It is for the most part near the surface of the ground, making it readily workable

[7] *Chem. & Met. Eng.* **31**, 468 (1924).
[8] *Chem. & Met. Eng.* **33**, 4 (1926).
[9] *Mineral Ind.* **33**, 660 (1925).
[10] *Eng. Min. J.* **123**, 695 (1927).

without the necessity of installing expensive equipment. The deposit was opened a few years ago by the Western Chemicals, Inc., but quarry equipment was relatively crude and entirely insufficient for large production. The company found itself in financial difficulties and was taken over by the Sodium Products Corporation. The plant was remodeled and now produces regularly approximately 120 tons per day.

The sulfate, relieved of an overburden of 2 to 10 feet of earth and clay, is drilled and dynamited and the fragments are loaded into trucks and hauled to the mill, where it is crushed. From a storage bin, the crushed ore then goes to a series of log washers, removing clay and other impurities. The ore then passes over two dewatering streams and goes to a rotary dryer. After leaving this dryer it is fed into a secondary crusher, where it emerges not over ¼ inch in size. It is then graded, and the first grade, consisting of ¼ inch fragments, goes to the pulp and paper industry. The second grade, under 10 mesh, goes to the glass industry and the third grade, under 20 mesh, is used by the manufacturers of stock remedies.

Soda Lake, California. A deposit has been worked for many years by the Consolidated Chemical Co., of Lompoc, Cal.[11] It is known as Soda Lake, in Carrizo Plain, San Luis Obispo County, Cal. The sodium sulfate available here for commercial utilization is said to be over a million tons. Transportation to the nearest railway station, McKittrick, involves a haul of 16 miles over a grade.

New Mexico. The Southern Chemical Co. of El Paso, Tex., did some experimental work on the production of anhydrous sodium sulfate in 1919 in Dona Ana County, New Mexico. The deposit lies about 25 miles west of Valmont between the San Andres Mountains and the white gypsum sands which are a prominent feature in the central part of the valley about 17 miles west of the railway. The roads between the deposit and the railway are reported to be fairly level, thus permitting hauling by motor truck. It is understood that water will generally rise nearly to the surface in any pits that are dug in the lower parts of this flat. This

[11] *U. S. Geol. Survey*, Bull. 717.

feature is important in considering the commercial value of the deposit, for the water standing in the pits and filling the pores in the solid material is naturally very nearly saturated with sodium sulfate at the temperature prevailing in the region. Such a solution should either be evaporated to yield all of its dissolved sodium sulfate, which would include any other soluble salts present in the water, or chilled to yield Glauber's salt, which could be sold as such or converted into the anhydrous salt.

These workings were later reported to have been taken under the control of the Great Southern Sulphur Co., of New Orleans. An application for commodity freight rates on the product was granted in April, 1919. The present rates are about $7.20 a ton to Kansas and Oklahoma points, $9.90 to Colorado, Missouri River points, and Galveston, $12 to Chicago, and $19 to Baltimore and New York.[12]

Great Salt Lake. It was stated in 1920[13] that the Minerals Salt Co. had been incorporated to work deposits of Glauber's salt on the South shore of the Great Salt Lake, from which the Midwest Dye & Chemical Co. had already produced some salt cake. These deposits were said to be 5 to 7 feet thick and under about 2 feet of sand. The method of working consisted in removing the overburden of sand and injecting live steam into the pits until enough solution was accumulated to be pumped into a small settling tank. This solution was then decanted into shallow ponds, where pure Glauber's salt separated as the solution cooled. It was later reported that both of these companies had discontinued active operations, but that other persons were studying methods of working the deposits.

The Utah Sodium Products Co., Salt Lake City, has acquired an option on 700 acres on the lake front to cover part of the same deposit. The deposits at the Gill Lakes, Natrona County, Wyoming, are worked commercially by the Gill Soda Co. They are about 12 miles northeast of Casper and about 7 miles from Fry station on the Chicago, Burlington and Quincy Railroad. The lakes are dry most of the year, but the deposits consist of Glauber's salt. The principal deposit, which is about 13 acres in extent, has been opened

[12] *U. S. Geol. Survey*, Bull. 717 (1923).
[13] *Chem. & Met. Eng.* **23**, 1245 (1920).

up to a depth of 22 feet in the solid salt, and preparations are being made to refine the material so as to make it suitable for all uses to which sodium sulfate is put. The Gill Soda Co. is producing Glauber's salt from the deposit near Sodium, Wyoming, which is about half a mile from both the Chicago, Burlington and Quincy and the Chicago and Northwestern railroads. The quantity available is estimated at more than 250,000 tons.

Canada. The Canadian output of natural sodium sulfate is small and has little promise of ever becoming a factor in the United States market.[14] Shipments in 1924 from Saskatchewan totalled 118 tons as against 733 tons in 1923. During 1924 Salts and Chemicals, Ltd., operated its plant at Sana, Sask., for the recovery of sodium sulfate from the bed of Muskiki Lake. The crude salts, running about 95 per cent hydrous sodium sulfate, are harvested in the winter months and placed on stock piles from which they are later treated in the company's drying plant on the property. The capacity of the plant is 100 tons of dried salt per day.[15]

A deposit of sodium sulfate near Palo on the Canadian National Railways transcontinental line west of Biggar, Saskatchewan, is being developed by the White Shore Chemical Co. of North Battleford. When a market has been established, a modern plant will be installed. The company has 1,500 acres under lease and hopes to increase this considerably. Another concern, the Sodium Sulphate Refining Co., Ltd., has been formed to develop sodium sulfate deposits located near Fusilier on the Canadian Pacific Railway, west of Kerrobert, Saskatchewan.[16] The plant of Bishopric & Lent Co., at Frederick Lake, also operated during 1924.

It is evident that natural sodium sulfate has received ample attention, scientifically, technically and commercially, as far as warranted. If it is not a factor in the general market the conclusion is that the cost of transportation is its insurmountable handicap. The experience of recent years has taught us the hopelessness of any development that is throttled by freight rates. It is safe to say that its market can only be local and very limited until con-

[14] *Mineral Ind.* **33**, 661.
[15] *Can. Mining J.* **45**, 1125 (1924).
[16] *Chem. & Met. Eng.* **34**, 266 (192').

ditions change. Some encouragement may be gleaned from the fact that the sales of natural sodium sulfate in 1926, 19,620 tons valued at $166,800, were about double the output of 1925.

Glauber's Salt

Nearly all of the country's supply of Glauber's salt comes from salt cake. The universal method of preparation consists in dissolving the cake in mother liquor, removing iron from the solution, clarifying and then crystallizing.

The dissolver is usually a circular lead-lined wooden tank, sometimes having a brick lining to protect the lead. A tank four feet deep and three feet diameter with two-inch staves and a ten-pound lead lining will serve for a twenty-ton daily output of crystal. The lead bottom at least should be covered with a course of acid brick. Heat is supplied by a one-inch open-end lead pipe reaching to the bottom. Mother liquor is run in through a two-inch lead pipe which dips down into the tank two feet. With steam at sixty pounds and the valve wide open, salt cake can thus be dissolved nearly as fast as one man can comfortably shovel and watch the temperature and specific gravity of the outflow. The liquor runs away through a two-inch side outlet placed six inches below the tank top. If the shovelling is regulated so that the dissolver is always about half full of salt cake and the temperature maintained for maximum strength by balancing the inflow of steam and mother liquor, the solution will leave quite uniformly saturated.

Dissolvers are sometimes placed on an upper level and the cake lifted in a bucket elevator but a preferred method is to have the dissolver on the ground level and to pump the solution to the purifying tanks. Two lead-lined tanks used alternately serve for this purpose. Into the solution is bucketed a slight excess of a thin paste of chloride of lime, previously prepared in a barrel, and then milk of lime is added to neutrality, the necessary stirring being done with a paddle. In a short time the precipitated iron has settled so that the clear solution can be run off to the crystallizers by means of side outlets and lead-lined movable launders.

The mud is washed once with water and settled and the clear solution run to the mother liquor storage. The wash constitutes

the water make-up for the process and its volume is such that the mud contains little value and is run away, although sometimes it is filter-pressed.

The crystallizers are wooden pans about twenty-five feet square and two feet deep, lined with ten-pound hard lead. A two-inch hole in the bottom, closed by a long wooden plug, connects each pan by a system of lead-lined launders to the mother liquor storage. When the solution has cooled to room temperature, the pan is drained and the crystal removed with care for the lead. After draining on a lead-covered floor it is packed in bags or slack barrels or piled in bulk for long storage. The latter is practiced in anticipation of extended hot spells, when the air is so warm night and day that there is no crystallization at all. All the natural ventilation possible is provided over the pans. This must be regulated by the windows, as rapid cooling with strong solutions yields needle crystal. There is a small demand for it and it is always stocked in cool weather but the bulk of the business calls for lump crystal.

In 1923 the Census of Manufactures reported a marketed production of 66,192 tons, valued at $1,521,000, from 21 establishments in this country. In 1925 the corresponding figures are 57,176 tons, valued at $1,255,570, from 20 establishments.

Anhydrous Sodium Sulfate

This is the pure grade sold for special uses, sometimes called anhydrous Glauber's salt. It is usually made by separating it out of its hot concentrated solution. This is done in a semicylindrical steel pan lined with lead, provided with mechanical lead-covered rakes that fish the salt up from the bottom. Direct heat is used under the pan. It can also be made by dehydrating Glauber's salt in a brick lined rotary furnace, internally heated with gas or oil. Another method, where only small lots are required, is to neutralize soda ash in a lead pan by vigorously stirring in the right quantity of concentrated sulfuric acid. The mass is practically anhydrous and requires only grinding. In 1923 the Census of Manufactures reported a marketed production from six establishments in this country of 3,183 tons valued at $267,500. The corresponding

figures for 1925 are 2,100 tons from five establishments, with a value of $128,115.

Sodium Sulfate, C. P.

This is usually made by recrystallizing a good grade of Glauber's salt and then dehydrating in porcelain evaporating dishes.

Uses of Sodium Sulfate

The principal uses for sodium sulfate are in the manufacture of glass, wood pulp, Glauber's salt, sodium sulfide, sodium silicate, sodium hyposulfite, smelter cake, barium sulfate, sodium aluminum sulfate, hog and cattle powders, and in dyeing. The largest consumption of salt cake is in glass manufacture but only an approximate idea of the distribution of the output can be obtained from available data. Thus, Glauber's salt is nearly all made from salt cake, the output of which has been mentioned as 57,176 tons for 1925. The same is true of sodium sulfide, the output of which was 18,366 tons in 1925. Hog and cattle powders account for some 3,000 tons of salt cake annually. Next to glass making, wood pulp makes the largest demand and that demand is on the increase particularly in Canada. Geological Survey Bulletin 717 states that the capacity of wood pulp plants using salt cake in this country is about 160,000 tons of pulp annually, compared with 180,000 tons for Canadian plants. The calculated quantities of salt cake required for the plants in the United States range from 22,000 to 56,000. A list of manufacturers of wood pulp who use sodium sulfate in this country is also given, as follows:

Atlantic Pulp & Paper Corporation, Savannah, Ga.
Bogalusa Paper Co., Bogalusa, La.
Brown Co., Berlin, N. H.
Central Paper Co., Muskegon, Mich.
E-Z Opener Bag Co., Braithwaite, La.
P. H. Glatfelter Co., Spring Grove, Pa.
Nekoosa-Edwards Paper Co., Port Edwards, Wis.
New York & Pennsylvania Co., Johnsonburg, Pa.
Pyne Tree Paper Co., Gordon, Ga.
J. & J. Rogers Co., Au Sable Forks, N. Y.
Southern Paper Co., Moss Point, Miss.

Stevens Point Pulp & Paper Co., Stevens Point, Wis.
Wausau Sulphate Fibre Co., Mosinee, Wis.
West Virginia Pulp & Paper Co., 200 Fifth Ave., New York City.

The following firms produced sodium sulfate as salt cake in 1920:[17]

Butterworth-Judson Corporation, 61 Broadway, New York.
Consolidated Chemical Co., Lompoc, Calif.
Contact Process Co., P. O. Drawer 98, Buffalo, N. Y.
E. I. duPont de Nemours & Co., Wilmington, Del.
General Chemical Co., New York City.
Grasselli Chemical Co., Cleveland, Ohio.
Kalbfleisch Corporation, 31 Union Sq. West, New York.
Charles Lennig & Co., Philadelphia, Pa.
Merrimac Chemical Co., 148 State Street, Boston, Mass.
Monsanto Chemical Works, St. Louis, Mo.
Southern Acid & Sulphur Co., St. Louis, Mo.
Hercules Powder Co., Wilmington, Del.
Mutual Chemical Co. of America, 99 John St., New York.
Naugatuck Chemical Co., Elm St., Naugatuck, Conn.
New Jersey Zinc Co., 160 Front St., New York.
Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.
Powers-Weightman-Rosengarten Co., Philadelphia, Pa.
Rollin Chemical Corporation, Equitable Building, New York.

The following firms produced Glauber's salts in 1920:[17]

Atlantic Carbonic Co., 268 Third St., Chelsea, Mass.
Chicago Copper & Chemical Co., 111 W. Jackson Boule., Chicago, Ill.
Columbus Crystal Co., 15 Arch Street, Newark, N. J.
Consolidated Chemical Co., Lompoc, Calif.
E. I. duPont de Nemours & Co., Wilmington, Del.
General Chemical Co., New York City.
Gill Soda Co., Cheyenne, Wyo.
Grasselli Chemical Co., Cleveland, Ohio.
Iowa Soda Products Co., Council Bluffs, Iowa.
Kalbfleisch Corporation, 31 Union Sq. West, New York City.
Charles Lennig & Co. (Inc.), Philadelphia, Pa.
Merrimac Chemical Co., 148 State St., Boston, Mass.
Powers-Weightman-Rosengarten Co., Philadelphia, Pa.
Stauffer Chemical Co., 624 California St., San Francisco, Calif.

[17] *U. S. Geol. Survey*, Bull. 717.

TABLE 17.—*Production of Salt Cake in the United States, 1923 and 1925.*[1]

	1923	1925
Number of establishments	34	35
Total production, tons	187,064	.....
For sale, tons	141,017	139,073
Value	$2,972,013	$2,315,502
Average value per ton	$ 21	$ 17

[1] Department of Commerce, *Census of Manufactures.*

Chapter IV

Principal Raw Materials and Finished Products—Specifications and Analysis. Domestic Production

Sulfuric acid, salt and nitre cake are the principal raw materials required for the manufacture of sodium sulfate and hydrochloric acid in the salt-cake furnace. In this chapter are given the specifications and methods of analysis for these raw materials and for the finished products, in the order named. Data on domestic production are also included.

Sulfuric Acid

Commercial 60 degree Baumé, 66 degree Baumé and 98 per cent sulfuric acid are the grades used. This acid is made principally from brimstone and is practically arsenic-free. Pyrites acid, unless very low in arsenic, should not be used, as the cost of removal of arsenic from hydrochloric acid will far exceed any ordinary price advantage in the sulfuric acid used. In special cases where certain impurities are permissible, waste sulfuric acid or "sludge acid" may be used to the advantage which its cost allows. Process and apparatus patents have been granted to Lasher for this purpose.[1]

Over 4,000,000 tons of sulfuric acid (100 per cent) are produced in this country annually and, of that, less than 3 per cent is used to make hydrochloric acid.

Salt

Sodium chloride is produced in very large quantities in this country both as rock salt from mines and by the evaporation of brine. The producing points are widely distributed geographically, the principal ones being located in the states of Michigan, New York, Ohio, Kansas, Louisiana and California. Their output in 1925 ranked in the order named. The total production of the United

[1] U. S. Patents Nos. 1,309,206; 1,337,141; 1,339,519.

States ranges between 6,500,000 and 7,500,000 short tons annually, of which about 150,000 tons are used for hydrochloric acid manufacture.

Mined salt is used for making hydrochloric acid. The quality is uniform, being generally 98.5 per cent sodium chloride. It is graded according to size thus: F.C., under 0.096 inch; C.C., 0.096 to 0.178 inch; No. 1, 0.178 to 5/16 inch; No. 2, 5/16 to 7/16 inch. No. 1 is the grade usually specified.

Salt for acid making is shipped and stored in bulk. Ordinary sheds with tight roofs will house it the year round without much caking. Unlike nitre cake, old salt piles can always be loosened with a pick.

Salt runs so uniform in quality that only incoming lots and monthly samples are tested. Generally the sodium chloride content is calculated by deducting from 100 per cent the determined content of moisture and insoluble matter.

Nitre Cake

Commercial sodium bisulfate or nitre cake is the by-product of the decomposition of sodium nitrate with sulfuric acid in making nitric acid. It contains all of the impurities of the raw materials which are not volatilized in the nitric acid still and in many cases an unnecessary quantity of dirt arising from careless handling. These impurities do not affect the quality of the muriatic acid unless they are exceptional (arsenic for example), but if the cake is not kept clean it will be found difficult to make 96 per cent salt cake from it. Nitre cake usually contains 35 per cent sulfuric acid but often varies three or four per cent either way. If not free from the nitrogen compounds that result from incomplete distillation in the nitric plant, free chlorine will be found in the muriatic acid.

In 1923 there were in the United States 45 establishments which made 154,087 tons of nitre cake and sold 129,447 tons at an average of $4.54.[2] The total nitre cake made, figured from the nitric acid produced, was about 145,000 tons, while the output of muriatic, if all were made from nitre cake, would have called for more than twice that amount. In 1925, 100,153 tons of nitre cake were made

[2] U. S. Dept. Commerce, *Census of Manufactures.*

for sale at a value of $394,833, or $3.94 per ton. The quantity consumed in the plants in which it was made is reported as 22,700 tons.[2]

At the value given, nitre cake is a very cheap raw material for muriatic acid, but much of it is produced in dynamite plants not favorably located for economic transport. In some of these places it is found best to throw it away. This is also done in large more centrally located nitric plants for lack of storage space during slumps in demand. Most of the quantity not reported sold in the Census of Manufactures can be accounted for by the consumption in the makers' plants for muriatic acid and salt cake or for soda alum or sodium sulfide and several other smaller uses. The nitre cake sold is principally used for the same purposes and, in addition, by paper and glass makers and for pickling iron.

Analysis of Nitre Cake

In order to calculate furnace charges in hydrochloric acid manufacture, the nitre cake used has to be regularly titrated for sulfuric acid content and a check is kept on the insoluble matter by occasional tests. Direct determinations of sodium sulfate content by barium precipitation are sometimes called for but generally the impurities are determined and the sodium sulfate is calculated by difference. Salt, sulfuric acid and insoluble matter are the impurities tested for. Salt and sulfuric acid are each close to 1.25 per cent and insoluble matter less than one per cent. Iron is sometimes determined and it generally runs under 0.25 per cent. Good cake may thus contain 96 per cent Na_2SO_4 but average salt cake is nearer 94 per cent. Sometimes salt cake is spotted with brown rust stains which are due to overheating of occasional lumps especially in hand worked furnaces.

American Chemical Society Standard Tests for Sodium Sulfate

The American Chemical Society Committee on Guaranteed Reagents has published [3] its recommended requirements and tests for sodium sulfate, as follows:

[2] U. S. Dept. Commerce, *Census of Manufactures.*
[3] *Ind. Eng. Chem.* **18**, 762 (1926).

Sodium Sulfate, Anhydrous

Requirements

Insoluble Matter—Not more than 0.010 per cent.
Loss on Ignition—Not more than 0.50 per cent.
Neutrality—To pass test.
Chloride (Cl)—Not more than 0.003 per cent.
Nitrogen Compounds (as N)—Not more than 0.0005 per cent.
Arsenic (As)—Not more than 0.0003 per cent.
Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.030 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.001 per cent).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Insoluble Matter—Dissolve 10 grams in 100 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° C., and weigh. The weight of the insoluble residue should not exceed 0.0010 gram.

Loss on Ignition—Weigh out about 2 grams, ignite at low red heat, and weigh. The loss in weight should not be more than 0.50 per cent.

Neutrality—To a solution of 5 grams in 50 cc. of carbon dioxide-free water add 3 drops of phenolphthalein indicator solution. No pink color should be produced (alkali), and on the addition of 1 drop of 0.1 *N* sodium hydroxide a pink color should be produced (acid).

Chloride—Dissolve 1 gram in 45 cc. of water; add 4 cc. of nitric acid and 1 cc. of approximately 0.1 *N* silver nitrate solution. The turbidity should not be greater than is produced by 0.03 mg. of chloride ion in 45 cc. of water after the addition of the quantities of nitric acid and silver nitrate used in the test.

Nitrogen Compounds—Dissolve 3 grams in 35 cc. of water in a flask; add 10 cc. of 10 per cent sodium hydroxide and about 0.5 gram of aluminum wire in small pieces. Allow to stand for 3 hours, protecting the flask from access or loss of ammonia. Decant 30 cc. of the clear liquid and add 1 cc. of Nessler's solution. The color should not be greater than is given by a quantity of ammonium chloride containing 0.01 mg. of nitrogen. Allowance may be made for nitrogen in the sodium hydroxide by treating 0.015 mg. of nitrogen in an ammonium salt with the quantities of water and reagents used in the test.

Arsenic—Determine the arsenic in 1 gram of the sample by the modified Gutzeit method. Special care in making blank tests is necessary in this determination.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Dissolve 5 grams in 75 cc. of water; add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 10 cc. of ammonium hydroxide. Allow to stand for 3 hours. If any precipitate is formed, filter, wash with water containing 2.5 per cent of ammonia, and dry. Mix the residue with about 0.02 gram of sucrose, ignite, and weigh. The weight of the ignited residue should not exceed 0.0015 gram.

Heavy Metals—Dissolve 2 grams in 25 cc. of warm water, add 2 cc. of hydrochloric acid, and boil gently for 10 minutes. Cool, neutralize to litmus paper with ammonium hydroxide, add 0.1 cc. of *N* hydrochloric acid, and pass hydrogen sulfide. No brown color should be produced (lead).

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is slightly alkaline. Any green color produced should not be greater than is produced by 0.02 mg. of iron in an equal volume of slightly alkaline solution to which hydrogen sulfide has been added.

Hydrochloric Acid

The commercial grades of hydrochloric acid are styled 18 degree, 20 degree and 22 degree Baumé. Only a small amount of the latter is made. Eighteen degree Baumé acid contains close to 27.75 per cent and 20 degree 31.25 per cent. Both grades are arsenic-free with respect to the requirements of the pure food law and contain no chlorine or at most a faint trace. The iron usually runs approximately 0.02 per cent and the sulfuric acid is generally required to be less than 0.1 per cent. Electrolytic acid, made from hydrogen and chlorine generated in electrolytic cells, is usually of better appearance than that made from nitre cake and, of course, contains no sulfuric acid.

Analysis of Hydrochloric Acid

For the determination of hydrochloric acid in plant work hydrometer readings used in connection with a table such as Table 1 are current practice. A correction of plus or minus one-thirtieth degree Baumé is made for each degree Fahrenheit above or below 60° for acid in the range of 18°-22° Bé. For more accurate determinations alkali titrations with allowance for acid impurities are used. Standardization of the alkali by titration with constant-boiling hydrochloric acid is recommended by Shaw [4] of the Mellon Institute. He describes a simple method for preparing standard samples which keep for years with practically no change. Bonner and Branting [5] have shown that constant-boiling hydrochloric acid at Salt Lake City where the average barometric pressure is 640 mm. contains 20.504 per cent HCl which is notably different from that determined for sea level (20.242 per cent).

The impurities usually determined in commercial acid are sulfuric acid, free chlorine, iron, nitric acid, total solids and silica, and arsenic. Details of these tests [6] follow:

[4] *Ind. Eng. Chem.* 18, 1065.
[5] *J. Am. Chem. Soc.* 48, 3093.
[6] Scott, *Standard Methods of Chemical Analysis.*

Sulfuric Acid is determined by evaporating 10 cc. on the steam bath, diluting with 10 cc. water, evaporating again and then titrating the residue with tenth-normal sodium hydroxide.

Free Chlorine: a 5 cc. sample of the acid is diluted to 10 cc., about 5 cc. of fresh starch solution added and a few drops of 5 per cent potassium iodide solution together with 1 cc. dilute sulfuric acid. A blue color indicates free chlorine. The color may be matched with a standard in a Nessler tube. It is possible to determine 0.0001 per cent Cl on a 5 cc. sample.

Iron is precipitated from a large sample and titrated with permanganate. Direct colorimetric determinations on the acid are not reliable because the yellow color is not all due to ferric chloride.

Nitric Acid is titrated with standard ferrous sulfate. A 5 cc. sample of the hydrochloric acid is cautiously added to 75 cc. of 95 per cent sulfuric acid, the sample being introduced under the surface of the latter. The mixture is now titrated. The ferrous sulfate test for nitric is delicate. Traces of nitric acid produce a pink coloration; larger amounts, a reddish brown to dark brown. The color is permanent when an excess of ferrous sulfate has been added.

Total Solids and Silica. One hundred cc. of the acid in a platinum dish is evaporated to dryness and the residue ignited and weighed. Five cc. of hydrofluoric acid is added with a few drops of sulfuric acid and the solution again evaporated and ignited. The first weight is total solids. The loss of weight in the second ignition is silica (SiO_2).

Arsenic.—The Gutzeit Method: Arsine is formed by the action of nascent hydrogen upon the arsenical compound, and the moist gas, freed from the hydrogen sulfide, is allowed to pass along the surface of a strip of paper sensitized with mercuric chloride solution. The arsenic forms a double compound with the mercuric chloride which has a characteristic yellowish-brown color. From the length and intensity of the color stain the amount of arsenic is estimated; a set of standard stains prepared in the same manner with known amounts of arsenic corresponds to the standard set of mirrors in the Marsh test. The best working range of the standard

stains with the size and form of apparatus described is from 0.001 mg. to 0.02 mg. As_2O_3.

The effect of iron upon the determination is of great importance as ferric compounds invariably inhibit the evolution of arsine. Ferrous compounds, on the other hand, by preventing polarization favor the evolution of arsine. Thus all iron must be reduced to the ferrous form before the test is made, and the same amount of iron in the ferrous form should always be present when running standards.

Apparatus

In Figure 1, *a* is a wide mouth bottle of about 60 cc. capacity. Two-ounce salt mouth bottles from Whitall Tatum Co. are satisfactory. Through a No. 4 one-hole rubber stopper is inserted a

FIGURE 1.—Gutzeit apparatus for the determination of arsenic.

glass tube *b* 7 cm. long and 1.25 cm. in diameter, constricted at the lower end so as to pass easily through the hole in the stopper. Through a No. 00 one-hole rubber stopper in upper end of *b* is inserted a second similar tube *c* of the same diameter but only 4 cm.

long. Finally through another No. 00 one-hole rubber stopper in the upper end of the second tube is inserted a glass tube *e* 4 mm. inside diameter, and 10 cm. long, constricted at a point 6 cm. from one end as shown in the sketch. The lower tube is used as a scrubber to remove hydrogen sulfide from the arsine; for this purpose there is placed in the tube before each test a strip of dry lead acetate paper. The upper tube is packed loosely with glass wool moistened with lead acetate solution. This serves the double purpose of removing any traces of hydrogen sulfide which may pass the lead acetate paper in *b*, and of keeping the arsine moist as it comes in contact with the sensitized test paper suspended in *e*, a condition essential to the success of the test.

Procedure

Ten grams of the sample are mixed with 25 cc. distilled water, 12 cc. "mixed acid" and ½ cc. stannous chloride solution. Boiling is continued until solution and reduction of iron is complete, shown by disappearance of iron color. The solution is washed into bottle *a*, diluted to 50 cc., and cooled. In the dried tube *b* is placed a strip of dry lead acetate paper and the glass wool in the tube *c* is moistened with lead acetate solution. The excess lead acetate solution is blown out of the tube. The dried tube *e* is put in place and a strip of sensitized paper suspended in it. Fifteen pieces of zinc are dropped into the bottle *a* and connections inserted at once. The bottle is shaken for a few seconds and placed in a water bath which is kept at a temperature within a few degrees of 75° F. After the test has run 30 minutes the sensitized paper is withdrawn from the tube, dipped in melted paraffine, and compared with the standard stains.

Reagents

Arsenic-free Hydrochloric Acid.—Commercial muriatic acid may be purified by treating with potassium chlorate so as to show no arsenic in the Gutzeit test.

Dilute Lead Acetate Solution.—A one per cent solution is prepared. If cloudy, acidify with just enough acetic acid to make a clear solution.

Lead Acetate Test Paper.—Sheets of qualitative filter paper are saturated with above lead acetate solution, dried at 100° C., cut into strips one inch square, fluted so as to fit the tube *b*, and preserved in corked bottles.

Zinc, C.P.: zinc, free from arsenic.—The pieces should not be larger than will pass a screen three meshes to the inch, nor smaller than will remain on a screen six meshes to the inch. Proper size may be obtained by specifying the size desired when ordering. The zinc is given a preliminary treatment in a casserole with dilute arsenic-free hydrochloric acid (1-1) until a dull gray clean surface is obtained. The zinc is then washed acid free and kept covered with distilled water and a watch glass.

Mixed Acid.—Dilute one volume arsenic-free sulfuric acid with 4 volumes of distilled water. Dissolve 10 grams of arsenic-free sodium chloride in each 100 cc. of the dilute acid.

Stannous Chloride Solution.—Dissolve 80 grams of stannous chloride in 100 cc. distilled water to which 5 cc. arsenic-free hydrochloric acid has been added.

Ferric-ammonium Alum Solution.—Dissolve 84 grams arsenic-free ferric-ammonium alum in one liter of distilled water to which 10 cc. "mixed acid" has been added. Ten cc. of this solution contains approximately the amount of ferric oxide present in the sample and this amount is used in the preparation of standard stains.

Sensitized Test Paper.—Swedish filter paper No. 0 is most satisfactory. Cut large sheets into four equal squares and dip into one-half per cent solution of mercuric chloride (0.5 gram $HgCl_2$ in 100 cc. water); the excess of solution is removed by a "squeegee" roller and the paper dried rapidly by spreading it on a flat hot cloth in a drying oven at a temperature of 100° C.; the paper should be turned over once during the drying in order to insure an even drying. The paper should be removed as soon as dry (as mercuric chloride is slowly volatile) and cut into strips 7 cm. long and 4 mm. wide. The large sheets should be trimmed on all four edges to a depth of one-quarter inch or more as the outer edges are often more concentrated. All of the paper should be cut the same width. A picture trimmer may be used to advantage. As soon as cut the paper should be bottled and sealed with paraffine until required for

use. A large supply should be made at one time, enough to last several months, and a new lot of paper should always be carefully standardized. Bottles containing sensitized paper should be carefully examined from time to time for a white deposit of mercuric chloride. If such a deposit is found the paper should be discarded. Such deposits are found on bottles containing paper which has been made up for some time and on bottles that have been subjected to high temperatures.

Arsenic Solutions for Preparation of Standard Stains.—One gram of resublimed arsenic oxide (As_2O_3) is dissolved in 25 cc. 20 per cent sodium hydroxide (arsenic-free), acidified with sulfuric acid, and diluted to one liter with recently boiled distilled water. One cc. of this solution *A* represents 0.01 mg. As_2O_3. By diluting 100 cc. of *A* to a liter with recently boiled distilled water, solution *B* is obtained, in which 1 cc. equals 0.001 mg. As_2O_3. These two solutions are all that are necessary in preparing the standard stains. The solutions change rapidly and should be made up fresh whenever standard stains are to be made. Glass-stoppered flasks should be used as containers.

Preparation of Standard Stains

The set of standard stains should contain color strips produced by 0.001, 0.002, 0.004, 0.006, 0.01, 0.015 and 0.02 mg. As_2O_3, respectively. The method of procedure is the same as for making the test. Before attempting to make any stains, the apparatus, solutions and zinc should be very carefully tested by running blanks. No appreciable stain should be formed in half an hour.

In running standard stains the proper number of cubic centimeters of solution *B* are added to the bottle from a 25 cc. buret together with ½ cc. of stannous chloride solution, and 10 cc. ferric-ammonium alum solution. The iron must be entirely reduced by boiling before the test is started. After reduction and cooling 15 pieces of zinc are added. The test is run for 30 minutes in water bath at a temperature within a few degrees of 75° F. The test paper is then dipped in melted paraffine and kept in a stoppered bottle away from light, heat, and moisture until ready for mounting.

Preservation of Standard Stains

Light, heat and moisture will produce rapid fading of the stains. An excess of moisture is added in making the stains by keeping in a water bath at 75° F. Great care is therefore necessary in mounting them. They are mounted on a piece of white paper using ordinary photo paste or mucilage. The paper is pasted into the form of a cylinder about 1 inch in diameter, the stains being on the outside of this cylinder. About 10 grams phosphorous pentoxide (P_2O_5) are placed in the bottom of a dry test tube 10 inches long and one inch inside diameter. The phosphorus is covered with a half inch layer of ignited asbestos. The paper on which the stains are mounted is placed inside the tube and on the asbestos. The top of the tube is finally drawn out and sealed. The stains should be kept away from light. A hydrometer case makes a satisfactory container.

Effect of Hydrogen Sulfide, Stibine and Sulfur Dioxide on Stains.—Hydrogen sulfide and stibine in sufficient quantity change the character of the stain. Hydrogen sulfide should be oxidized with potassium permanganate before running the test. Antimony if present in excess of 0.002 per cent Sb_2O_3 will affect the character of the stain causing it to be longer and lighter in shade. Such a stain if subjected to fumes of hydrochloric acid will fade distinctly while a pure arsenic stain is intensified. The same holds for stains obtained from combination of hydrogen sulfide and arsine. Sulfur dioxide, if present, reacts with hydrogen forming hydrogen sulfide.

Precautions in Operating

The rate of evolution of hydrogen and arsine is influenced by the amounts of arsenic and iron present; an increase in either or both of these constituents favors the more rapid evolution of hydrogen. Within the limits between which iron and arsenic are present, with rare exceptions, there will not be sufficient variation in the rate of evolution of hydrogen to affect the result seriously. If it is suspected that the action is too slow, a second strip of sensitized paper should be put in at the end of the first half hour and run for a second half hour. If more than a mere trace is obtained it is

better to repeat the analysis, accelerating the action by introducing about 0.03 gram of ferric oxide (Fe_2O_3, in the form of arsenic-free ferric-ammonium alum) before reducing with stannous chloride. If for any reason the action is too violent, so that the stain produced is "thin" and not of the right color or density, the analysis should be repeated, cooling the sample to a lower temperature. It is only in exceptional instances, however, that other than a normal action will be obtained.

Blank tests should be run frequently to insure freedom from arsenic. The glass wool in *c* should be moistened with dilute lead acetate solution before each test so that the gas shall be uniformly moist, one of the fundamental requirements of the test. The amount of zinc, acid, and total volume in *a* should always be approximately the same. It is extremely important that the evolution of gas from the zinc be always as nearly uniform as possible. If the arsenic is carried over too slowly the color band is denser and too short, as compared with the standard for the same amount. Tubes *b* and *e* should be dried after each test. The sensitized test paper should always be kept dry and away from light and heat. At the end of the run it sometimes happens that a slight sublimate is seen on the inside of tube *e*. This is without influence on the result, but the tube should be cleaned with dry cotton before being used again. Uniformity of conditions in the preparation of standards and in the running of actual tests is essential for accurate work. Any number of determinations may be made at the same time; it is necessary, however, that all apparatus shall be of the same size. Paraffine should be kept clean and free from water. The stannous chloride reduces ferric to ferrous and arsenic to arsenious compounds. It is only by reducing both of these entirely before the test is started that proper results can be obtained. When ferric compounds or arsenates are present the stains are always too short.

American Chemical Society Standard

The requirements and tests for hydrochloric acid as recommended by the American Chemical Society's Committee on Guaranteed Reagents are as follows:[7]

[7] *Ind. Eng. Chem.* **17**, 756 (1925).

Hydrochloric Acid

Requirements

Appearance—Colorless and free from suspended matter or sediment.
Strength—Not less than 35 per cent by weight of HCl.
Nonvolatile Matter—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.0002 per cent.
Free Chlorine (Cl)—To pass test (limit about 0.0002 per cent).
Sulfite (SO_3)—Not more than 0.003 per cent.
Arsenic (As)—Not more than 0.00001 per cent.
Iron (Fe)—Not more than 0.0001 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble material would interfere.

Appearance—Mix the material in original container, pour 10 cc. into a test tube (150 mm. by 20 mm.), and compare with distilled water in a similar tube. The liquids should be equally clear and free from suspended matter and on looking across the columns by transmitted light there should be no apparent difference in color between the two liquids.

Assay—Tare a small glass-stoppered Erlenmeyer flask containing 15 cc. of water. Quickly introduce about 3 cc. of the acid, stopper, and weigh. Titrate with standard sodium hydroxide solution.

Nonvolatile Matter—Evaporate 85 cc. of the acid to dryness in platinum after addition of a drop of sulfuric acid, ignite at cherry redness for 5 minutes, cool, and weigh. The residue should not weigh more than 0.0005 gram.

Sulfate—Add 0.01 gram of sodium carbonate to 20 cc. of the acid, evaporate to dryness, take up with water, filter, and make up to a volume of 10 cc. in a test tube. Add 1 cc. of hydrochloric acid (1 volume strong acid in 20) and 1 cc. of 10 per cent barium chloride solution. The turbidity after 10 minutes should not be greater than is obtained in an equal volume of distilled water containing 0.01 gram sodium carbonate neutralized with hydrochloric acid, 0.05 mg. of sulfate (SO_4), and the quantities of hydrochloric acid and barium chloride used with the sample.

Free Chlorine—To 25 cc. of the sample add 25 cc. of freshly boiled water and cool; add 2 drops of 2 per cent potassium iodide solution and 1 cc. of carbon disulfide, and mix. The carbon disulfide should not acquire a pink color in half a minute. The potassium iodide should be free from iodate.

Sulfite—Add 0.05 cc. of 0.1 *N* iodine solution and a few drops of starch solution to 50 cc. of water, and then add 5 cc. of the sample previously diluted with 50 cc. of water. The mixture should retain a blue color after mixing.

Arsenic—Determine in 20 cc. of the sample by the Gutzeit or the Marsh-Berzelius method. Special care in making blank tests is necessary in this determination.

Iron—To 85 cc. of the sample add about 0.05 gram potassium nitrate and evaporate to a volume of about 2 cc. Wash into a color comparison tube, add 2 cc. of 5 per cent ammonium thiocyanate solution, and stir well. Compare with a solution of the same volume containing 1 cc. of hydrochloric acid and the quantities of potassium nitrate and ammonium thiocyanate used in the test, to which standard ferric chloride solution is carefully added from a buret until the tints match.

Heavy Metals—Evaporate 10 cc. of the acid to dryness, add 5 drops of hydrochloric acid, dilute to 50 cc., and saturate with hydrogen sulfide. No color should be observed.

Hydrochloric Acid, C.P.

Electrolytic hydrogen chloride absorbed in distilled water yields acid of the grade called "C.P." or reagent chemicals for laboratory and medicinal use. They are not strictly chemically pure; the small percentage of the various impurities which they contain are usually printed on the labels. Chemicals of this grade conform with pharmacopeia requirements. The great proportion of C.P. hydrochloric acid has always been made by the fractional distillation of commercial acid. This is carried on in so-called "boilers" which are horizontal chemical stoneware cylinders, in the lower side of which are fitted long glass test tubes. The boilers are so set over small oil-fired brick furnaces that only the tubes are exposed to the heat.

Flue Gases

The hydrochloric acid in the flues entering and leaving the absorption system is determined by aspirating a measured volume through a flask fitted with a tube filled with glass beads and dipping into the absorbent just enough to draw sufficient up into the tube to thoroughly scrub the gas. The absorbing medium may be either water or dilute sodium hydrate. When care is used in adjusting the little scrubbing column water effects complete absorption and the acidity is easily obtained by direct titration.

Chapter V

Salt Cake Furnaces

By far the most important feature of this book is the description of the salt cake furnace and its operation. As explained in Chapter I, the decomposition of salt by sulfuric acid for the formation of salt cake and hydrochloric acid takes place in two steps, in the first of which the acid sodium sulfate is formed. Whether this first step is performed in a separate vessel, as it may be, or whether both steps are performed in the salt cake furnace, the latter is the principal part of the equipment. It is the most expensive part to build as well as to operate. All other parts of the process have waited on the development of the furnace. Thus the story of the furnace is the story of the manufacture of hydrochloric acid and salt cake.

Hand-worked Reverberatory Furnaces

For many years alkali was all made by the LeBlanc process. Its first operation is the preparation of salt cake. In the early days, LeBlanc made it in a simple reverberatory furnace. Salt and acid were mixed on the hearth and the flue gas from the coal fire on the adjacent grate passed directly over the charge, rapidly effecting conversion and sweeping the hydrogen chloride up the stack. In England the law abated this nuisance by the establishment of a permissible minimum of acid in the escaping gas. To comply, the manufacturers drew the gas up large towers built of stone slabs and packed with coke, through which water was trickled. As uses developed for all of the hydrochloric acid, the design and operation of the towers were modified, but the methods adopted did not yield a product of the strength and purity obtainable in muffle furnaces. Moreover a demand came for salt cake of a quality also thought obtainable at the time only in a muffle.

Pot-and-Muffle Furnaces

The first muffle furnaces were hand worked, like the reverberatories, but with them came the addition of the pot in which the first step of the reaction was performed. Pots had been attached to open fired furnaces in some instances, but the standard for many years was the pot-and-muffle furnace shown in Figure 2. Although these furnaces are nowadays rarely built some are still in use.

The typical furnace is built of red bricks and fire-bricks with sixteen-inch walls heavily stayed. The walls around the fire box are further strengthened by a covering of cast iron plates an inch thick. The grate is 6 feet by 4 feet, the muffle 8 feet by 20 feet, and the saucer-shaped cast iron pot 10 feet diameter by 2 feet deep. The dome over the latter is built of red brick. The muffle floor is made of rabbitted fire tile sized to span the walls forming the bottom flues; the arch of the muffle is sometimes made of rabbitted fire tile, but hard burned fire-brick laid to form an arch 4½ inches thick also makes a good job and costs much less. The flue gas first passes through the broad space between the arches over the muffle; this space is a foot high; it then returns through the outside bottom flues and doubles back through the center bottom flues under the pot and to the stack. Oil or gas are used when convenient but coal is the usual fuel and the amount for a ton of salt cake is 1000 pounds. It is sometimes burned with a forced draft (induced by a blower) in order to prevent acid loss up the stack through the ever-occurring leaks in the muffle arch. This loss often amounts to one-tenth of a gram per cubic foot of flue gas or higher, but it is usually about 0.002 gm.

Many variations in this arrangement have been tried but always with questionable advantage. At the Butterworth & Judson plant recently dismantled in Newark, N. J., there was a large muffle to which four pots were attached.

The Oehler-Meyer Process. The Oehler-Meyer process [1] uses only a muffle, without any pots at all. Bisulfate is used for decomposing the salt; the two are mixed and ground to a fine powder and then heated in a muffle without any stirring or working for the

[1] U. S. Pat. 702,877.

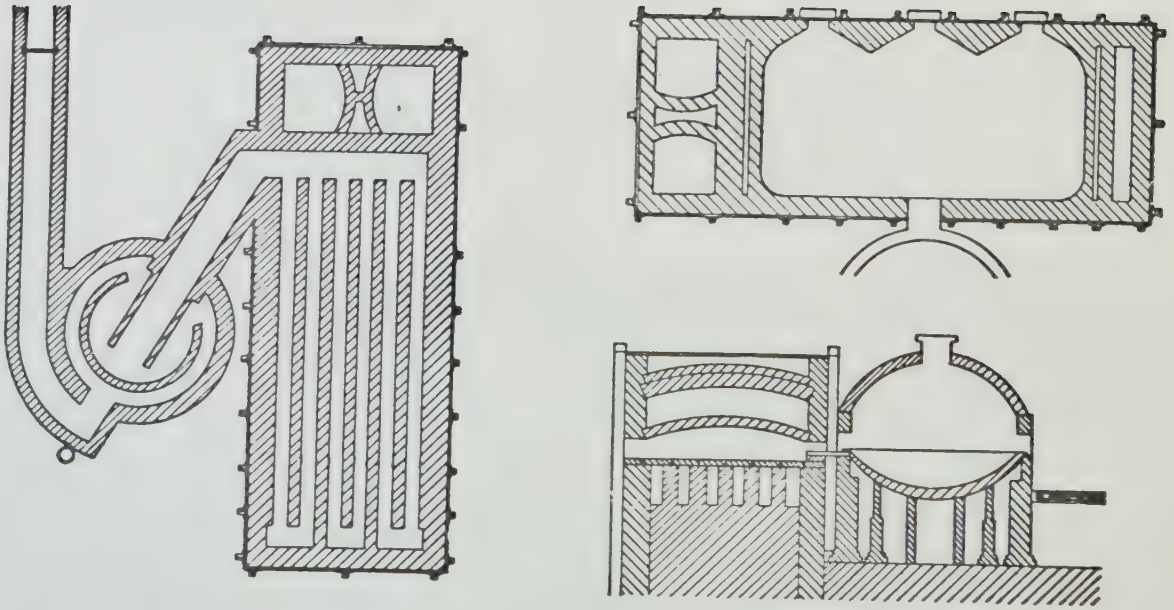

FIGURE 2.—Pot-and-muffle furnace, showing plan of flues, plan of muffle and vertical section of pot and muffle.

extended period of three charges in twenty-four hours. The temperature of the cake must be 450° to 500° C. The method is not familiar in this country. It doubtless makes good salt cake but at low capacity of muffle area. The bisulfate may not exceed 3 per cent moisture or it causes caking to such an extent that the charge requires stirring. The author made a trial of the method for a month, in an ordinary furnace with the pot blanked off, to see if it could be worked with relatively coarse material and a minimum of stirring. Salt and 30 per cent bisulfate were ground together to screen 10 per cent through 100 mesh, 30 per cent through 30 mesh, 80 per cent through 40 mesh and 100 per cent through 10 mesh. The muffle area was 130 sq. ft. and by forcing the fire, charges of 2800 pounds of bisulfate and 1000 pounds of salt were converted to good salt cake in four hours, with thorough stirring every half hour. The same furnace on salt and acid decomposes four tons of salt and produces five tons of salt cake in twenty-four hours.

Operation of Pot-and-Muffle Furnace. The regular method of working a standard pot-and-muffle furnace with a muffle area of 180 sq. ft. is to charge 1250 pounds salt and 1130 pounds of 98 per cent sulfuric acid (or its equivalent in lower strengths down to 60° Bé.) into the pot every three hours. The salt is put in first and stirred by hand while the acid flows in through an aperture in the dome. The charging occupies about fifteen minutes; towards the end the reaction has started and the mixture may foam over through the charging door unless the addition of the acid and the heat have been regulated to keep the temperature of the mixture below 200° F. The door is closed and the heating regulated so as not to exceed 300° F. Near the end of the three-hour period the charge is pitched through the tile door between the pot and the muffle with a long handled iron paddle worked through the pot door by the pot man, while the muffle man spreads it evenly over the muffle floor. In the muffle the material is sliced or broken up and stirred every half hour and finally drawn out in time to receive the next pot charge. The pot charge when pitched contains about 17.5 per cent sulfuric acid and is a trifle sticky. From the muffle, if the heating has been uniform and sufficient, the hot cake as drawn has a lemon yellow color which slowly disappears on cooling. Local

overheating may occur in spots, resulting in the decomposition of the slight amount of sulfate of iron present as an impurity; the ferric oxide thus formed stains the product to its disadvantage. Under-heated cake has a very noticeable grayish color. If the ingredients are correctly proportioned in the charge the color of the finished cake is a sure guide to its quality so that pyrometers are rarely used. A close laboratory check on the salt and acid in the cake is of course indispensable.

Two men work one furnace and it is a hot, hard, gassy job. Some years ago five full charges could be finished in a twelve-hour shift but now it is hardly possible to get men to do this unpleasant work at all. This is one reason why the furnace is being rapidly abandoned.

Repairs are low as they consist mainly of relining the fire box and cementing up cracks in the muffle arch. It is rarely necessary to completely rebuild the latter. The pot is an expensive casting and the job should be well done. When in service, attention should be paid to the addition of the acid or a hole may be eaten through the iron in a short time. The pots are two inches thick at the bottom and have a slight taper up to the rim.

Part or all of the acid charged to the pot may be replaced by bisulfate of soda. Sometimes the latter is used cold, being merely coarsely broken up and mixed with the salt, but the time consumed in heating up this mixture to the reaction temperature lowers the furnace capacity so that it is customary to charge the bisulfate in molten form. For this purpose a "soup pot" is used. This is a heavy cast-iron vessel of oblong outline and somewhat rounded bottom set in brick work over a small grate. It is elevated so that the molten bisulfate may flow easily to the furnace pots through cast iron or steel launders. A typical charge consists of 860 pounds salt, 420 pounds 98 per cent sulfuric acid and 1000 pounds 36 per cent bisulfate.

Hydrochloric Acid Retorts

Salt is decomposed with sulfuric acid in cast-iron retorts (Fig. 3) to produce hydrochloric acid and bisulfate of soda. These may be operated intermittently, the salt being first charged and the retort

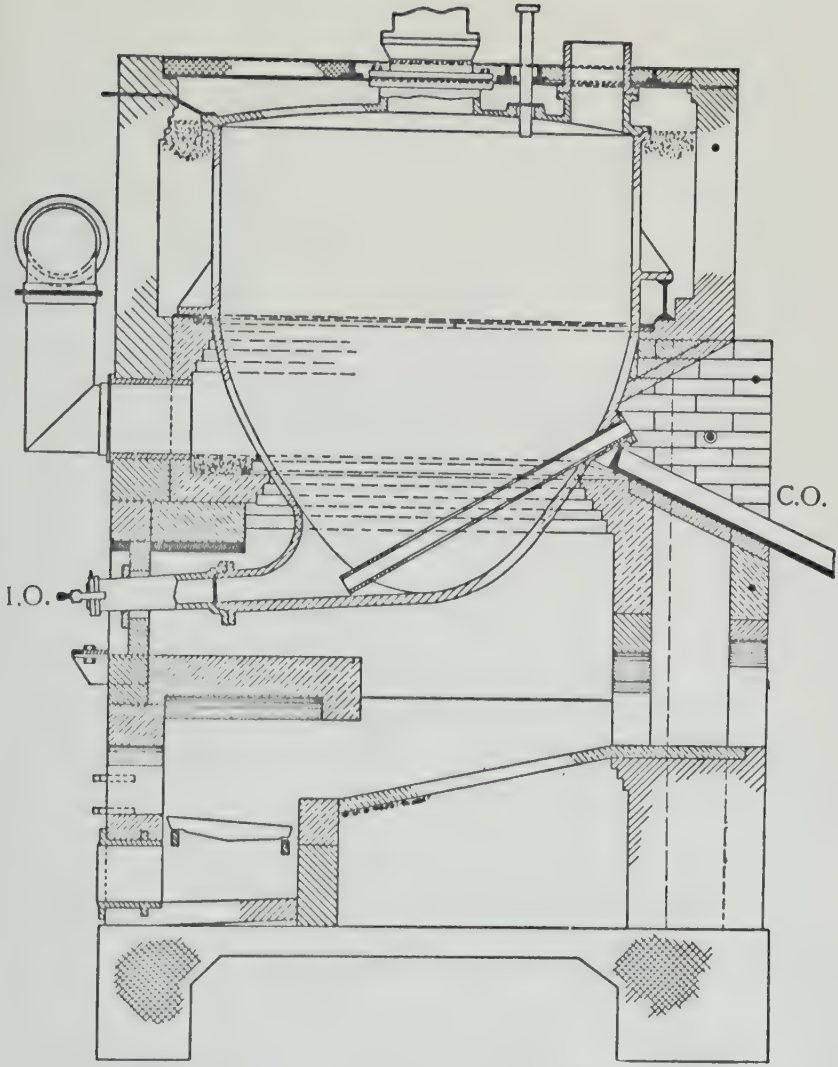

FIGURE 3.—Retort for continuous or intermittent charging. Vertical section.

closed, then a measured quantity of acid run in from a measuring tank through a small trapped inlet. A retort of standard size, 9 ft. deep by 8 ft. diameter, takes three tons of salt to a charge and as much as two charges may be distilled in twenty-four hours.

The bisulfate is discharged through the bottom outlet *I.O.* into cooling pans.

When the bisulfate outlet is arranged as shown at *C.O.* these retorts may be continuously operated, a molecular proportion of salt and acid being constantly fed through the cover while a corresponding quantity of bisulfate overflows. This method yields a larger output but its principal advantage lies in the continuous and uniform discharge of bisulfate which can thus be taken directly into mechanical salt cake furnaces or cooled by mechanical means into small forms such as scales or pearls to save the expense of crushing before using.

Cast-iron water-cooled cones or cylinders are used for this purpose. In the former case the bisulfate flows onto the rotating cone, and in the latter the horizontal slowly-rotating cylinder dips into a shallow pan of molten bisulfate. The thin scale is scraped off by a firmly fixed knife. There is some difficulty in scraping off the scale unless a fine spray of cold water is applied to the metal surface just before it dips into the bisulfate. When worked continuously retorts distil off the gas in a small uniform stream so that it can be absorbed in much smaller and cheaper equipment. The constant volume of molten bisulfate held in the retort serves as a heat reservoir that keeps the reaction uniform. After a shutdown the bisulfate can be slowly melted again before starting to charge, if this is preferred to emptying the retort through the bottom outlet.

Zahn & Co., Ltd., of Berlin have patented the process of using such a bisulfate heat reservoir for the non-continuous operation of retorts but the possible advantage of the method has not been demonstrated in this country.

The same company has also patented a form of continuous retort called a "bisulfate boiler," which is merely the usual retort with the cover replaced by a brick arch built so as to form a relatively large square chamber. This has the advantage that 60° Bé. sulfuric acid may be used instead of 66° Bé. which is generally used in retorts with cast iron covers. It is doubtful if the loss of gas through leaks in this arch would make up for the relatively slow corrosion of the cast-iron covers on retorts charged with the weaker acid.

Mechanical Furnaces

According to old records and patent files almost every possible form of mechanical furnace was tried in England years ago for making salt cake. Among the earliest were horizontal rotary cylinders both for internal and external heating. Hazelhurst's furnace, patented in England in 1882, was an externally heated cylinder rotating on hollow trunnions. The salt was charged through a manhole in the side; the acid was introduced through one of the trunnions and the gas distilled through the other. Walker's furnace, patented in England in 1887, was an internally fired rotary consisting of two independent cylinders communicating with each other and each performing one of the two steps of the salt and acid reaction. Dr. Edward Hart worked his pyrosulfate process [2] in a rotary similar to Hazelhurst's but provided with an internal scraping device to prevent the charge from sticking to the sides.

None of these rotaries was successful. When the charge is about half finished it is plastic and sticks to the shell where it gradually bakes hard; it is not practicable to scrape it off and the metal, thus prevented from transmitting the heat, soon buckles and burns through if the furnace is fired externally. The difficulty with the internally heated rotaries was the same as has already been mentioned in connection with the internally heated reverberatories, that is, the early absorbing equipment was not adapted to making strong muriatic acid from the dilute gas which these furnaces yield, and the salt cake was contaminated with dust from the coal fires. An improved form of rotary now in successful use is described later on.

Mactear's furnace,[3] an English invention (Fig. 4), was a shallow revolving cast iron pan internally heated; it was charged at the periphery. Revolving plows located on a fixed radius of the pan circle but each rotating on its own axis moved the cake toward the center discharge. In spite of its relatively complicated mechanism and consequent high repair costs, this furnace was used for a long time. At least one was in operation in this country as late as 1910.

In 1912 J. H. Nield patented [4] an oblong mechanical muffle in

[2] U. S. Pat. 698,709.
[3] U. S. Pat. 253,734.
[4] U. S. Pat. 1,033,825.

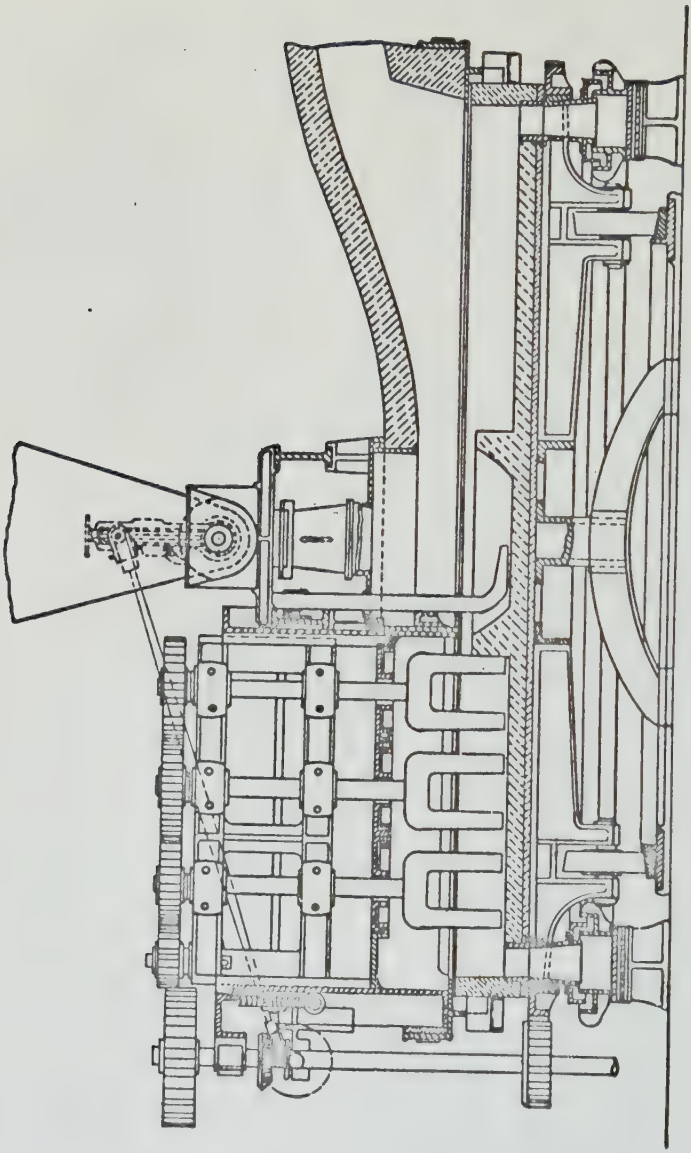

FIGURE 4.—Mactear's direct fired circular mechanical furnace.

which the device for moving the cake to the discharge end had a reciprocal motion. His process [5] of mixing a small amount of finished cake with the fresh charge was intended to counteract its tendency to stick and to facilitate its movement across the hearth. Figure 5 is a cross section of this furnace showing the method of moving the plows back and forth on the hearth by means of a rocker

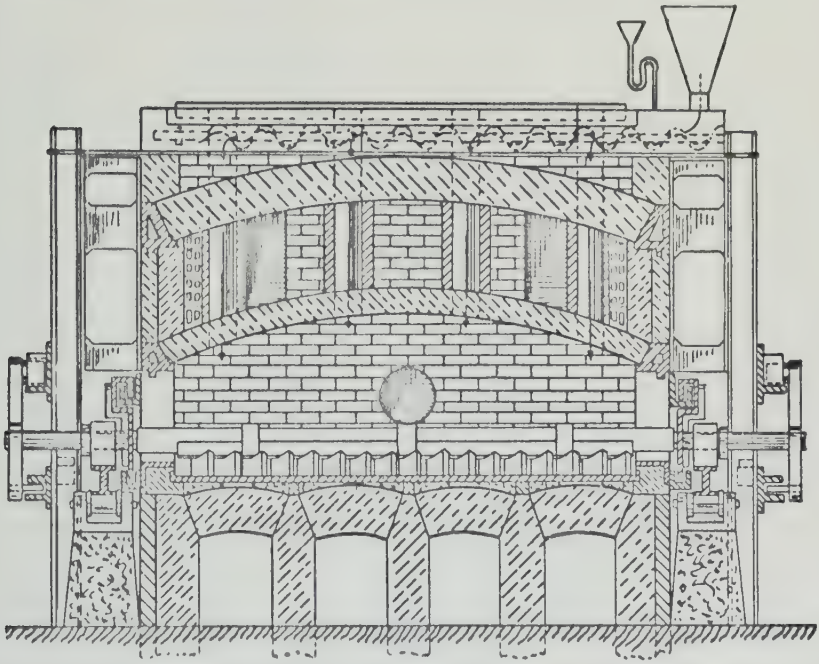

FIGURE 5.—Vertical cross section of Nield's oblong mechanical muffle furnace.

shaft actuated by a rack and pinion on a slide arrangement running along each side.

An oblong mechanical muffle (Fig. 6) was patented by Skinner in 1923.[6] This differs from Nield's design in that the scrapers have a rotary motion and one end of the muffle floor is depressed so that salt and acid can be charged directly. As the first step of the reaction progresses the solidified material is moved up onto the level floor and the operation is continuous. One of these furnaces

[5] U. S. Pat. 1,102,539.
[6] U. S. Pat. 1,467,509.

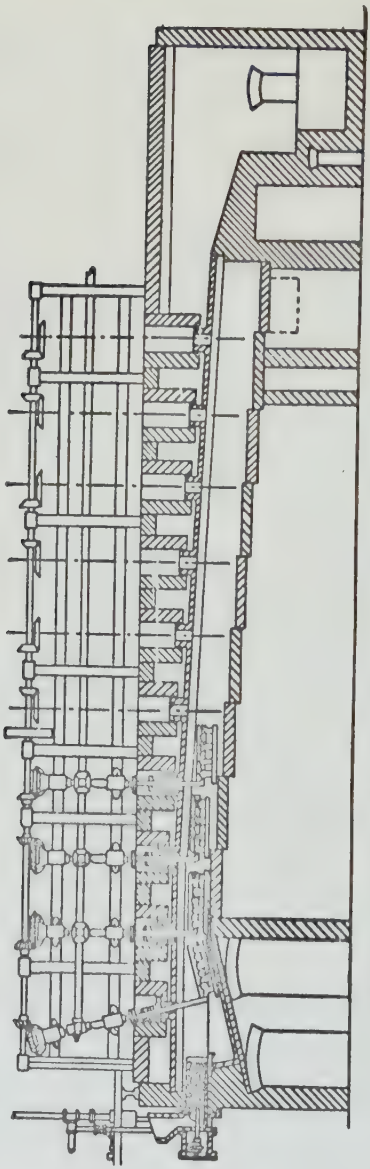

FIGURE 6.—Skinner's oblong mechanical muffle furnace—longitudinal section.

was built by the old Western Chemical Company in Denver. Difficulties to be expected with a muffle of that shape and with such a complicated stirring device would be high repair costs to the mechanism and the arch, loss of gas by leaks through the arch, and the loss of time for necessary cleaning of the stirring arms and plows.

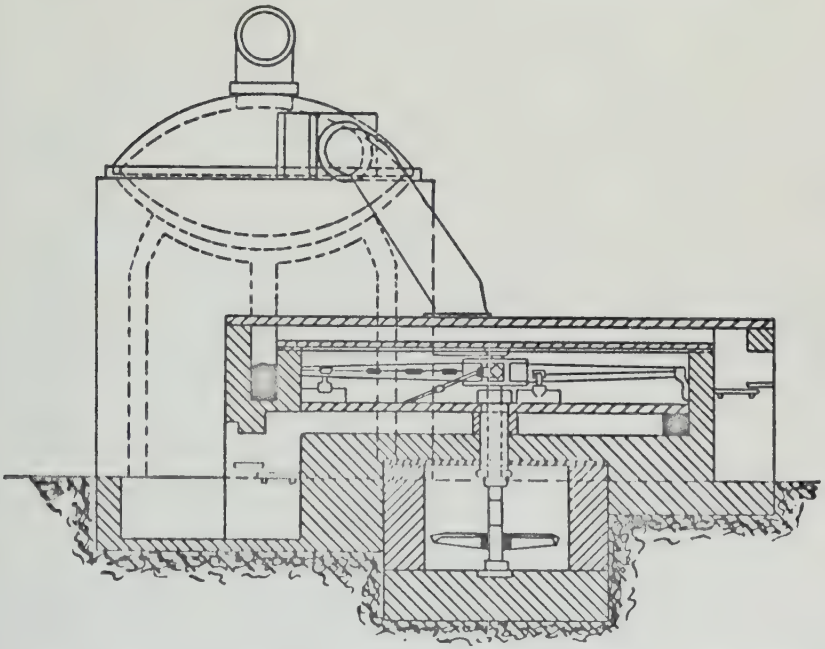

FIGURE 7.—Black & Larkins furnace. First circular mechanical muffle furnace. Longitudinal section.

Six and Guttman's furnace,[7] also an oblong mechanical muffle, is reported to be in use in England by the Stavely Coal & Iron Co., Ltd. According to Cumming [8] the nitre cake and salt are ground and mixed and then charged into one end of the muffle which is floored with cast-iron plates. The rabbling is done by two sets of tool-steel rakes attached to two main rods that project from one end of the furnace where they are mechanically driven fore and aft.

It is of interest finally to mention the furnace of Black and Larkin,

[7] Brit. Pat. 4226 (1915).
[8] Lunge & Cumming, *Hydrochloric Acid & Salt Cake*, p. 188.

patented in 1882 [9] (Fig. 7). This is the first circular mechanical muffle. The muffle has a cast-iron top and bottom and brick-work sides and is encircled with heating flues. The cake is moved by means of plows on horizontal arms fixed to a central rotating shaft. The best known make of this type and the one in common use in this country is the Mannheim which is described below.

Modern Circular Mechanical Muffle Furnaces

The Mannheim furnace originated in the plant of the Verein Chemischer Fabriken in Mannheim, Germany.[10] It is built in this

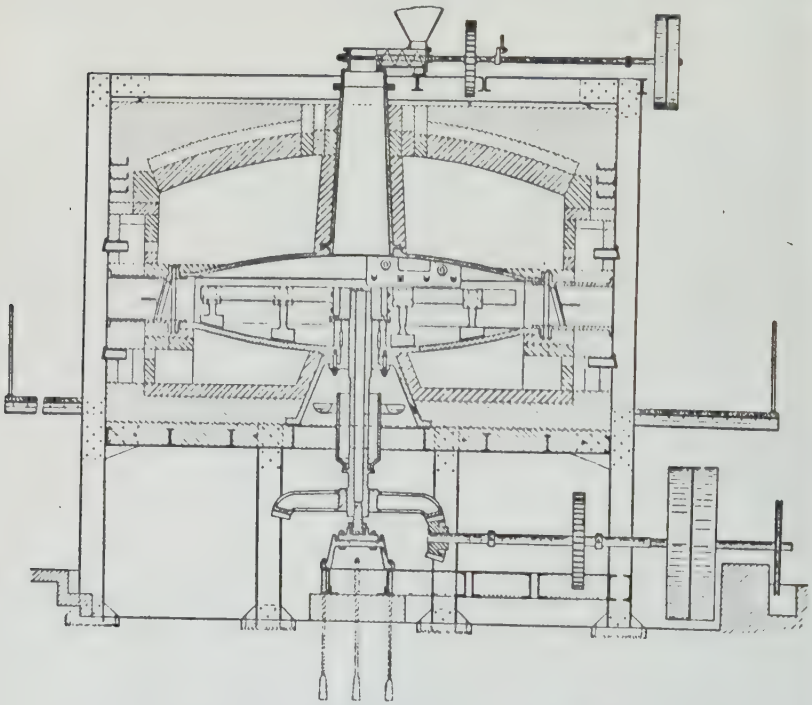

FIGURE 8.—Mannheim furnace. Vertical section.

country by the Bethlehem Foundry and Machine Company, in Bethlehem, Pennsylvania. Figure 8 is a vertical cross section of this furnace, which is an improvement in detail over the old Black and

[9] U. S. Pat. 253,734.
[10] Brit. Pat. 16207 (1902).

Larkin furnace. Its original purpose was for use on salt and bisulfate, but salt and 66° Bé. sulfuric acid may also be fed to it. If only 60° Bé. sulfuric acid is available it should first be converted to bisulfate in a retort.

When acid is used it is admitted in a continuous stream through a small trapped pipe with a funnel-shaped inlet. This pipe enters the top of the large central charging flue into which the salt from the feed hopper also enters. When bisulfate is used it is ground and mixed with the salt and charged through the hopper. The mixture thus starts at the center of the pan and is worked towards the periphery where it leaves the furnace automatically and drops into a car.

There is a cast-iron gas outlet line on the cover which is lined with fire tile, and a fire box attached to one side of the furnace.

Asbestos rope is used in all the cast-iron muffle joints, which with careful bolting gives a good tight job. The top arch is made of fire-brick laid dry and wedged by driving steel plates into the larger interstices, and finally all the joints are filled with fire-clay grouting. If well built the arch will last for years. Both the cast-iron charging inlet and the gas exit pipes require the protection of a well tied-in single course of fire brick. When properly installed the mechanism can be rotated by hand. It is lubricated with graphite and the steel pin at the bottom of the shaft as well as the button in the step are case hardened. The stationary scraper attached to the lugs on the pan cover is intended to keep material from accumulating on top of the rotating arms. The scrapers are placed in 4 inch by 4 inch pockets in the scraper arms; they slide loosely in the pockets and move up and down over the irregularities of the pan bottom. Cast-iron caps over these pockets prevent the scrapers from rising too high. The scrapers are made of cast-iron, stoneware and various other materials have been tried but without improvement. If time permits, it is best to fire the furnace slowly with wood for four weeks to dry it out properly, meanwhile giving required attention to the iron stays and keeping the mechanism in motion.

The furnace is started by putting 4,500 pounds of finished cake into the muffle while the mechanism is in motion and slowly

firing until the contents have assumed a yellow color and a woolly consistency; then regular charging is begun after setting the feed screw to admit 750 pounds per hour of a mixture which is carefully proportioned. This corresponds to a twenty-hour consumption of 13,000 pounds of bisulfate and 5,000 pounds of salt and produces roughly 14,000 pounds of salt cake. This is the capacity of the standard unit which is 11 feet in diameter but some are built up to 18 feet in diameter. In the latter only the center part of the pan bottom is made of cast iron, the balance being formed of tile.

The furnace must be shut down at intervals of not more than two months for cleaning and repairing. It takes five days to cool and clean and then resume operating. The scrapers near the periphery wear fastest, the two nearer the center last about three months and the outer two wear out in about two months. The controlling temperature is that of the gas in the flue above the muffle; it should be kept close to 840° F. The furnace drive requires three horsepower. The life of the muffle is under two years or equivalent to an output of 4,500 tons of salt cake. The draft on the muffle is regulated by analysis to 30 per cent by volume of hydrochloric acid.

To obtain a passable product it is imperative that the raw materials be finely ground and thoroughly mixed mechanically, and especially that the proportions be accurately controlled by analysis. Forcing the firing to the extent required to obtain a good product at the normal rate results in high repairs for rakes and pan so that the average quality does not meet the requirements of particular customers. In consequence, Mannheim furnace cake mostly goes into the manufacture of other salts in the plant.

There are various patented devices for feeding these furnaces, the purposes of which are mainly the prevention of excessive wear and the improvement of quality of product. Notable among them are those of Howard,[11] Krickbaum,[12] and Dietz and Latten.[13]

Howard employs a separate circular cast iron pan equipped with a stirring device so placed above the furnace that the well mixed

[11] U. S. Pats. 1,145,897; 1,145,898; 1,193,552.
[12] U. S. Pat. 1,167,763.
[13] U. S. Pat. 1,485,488.

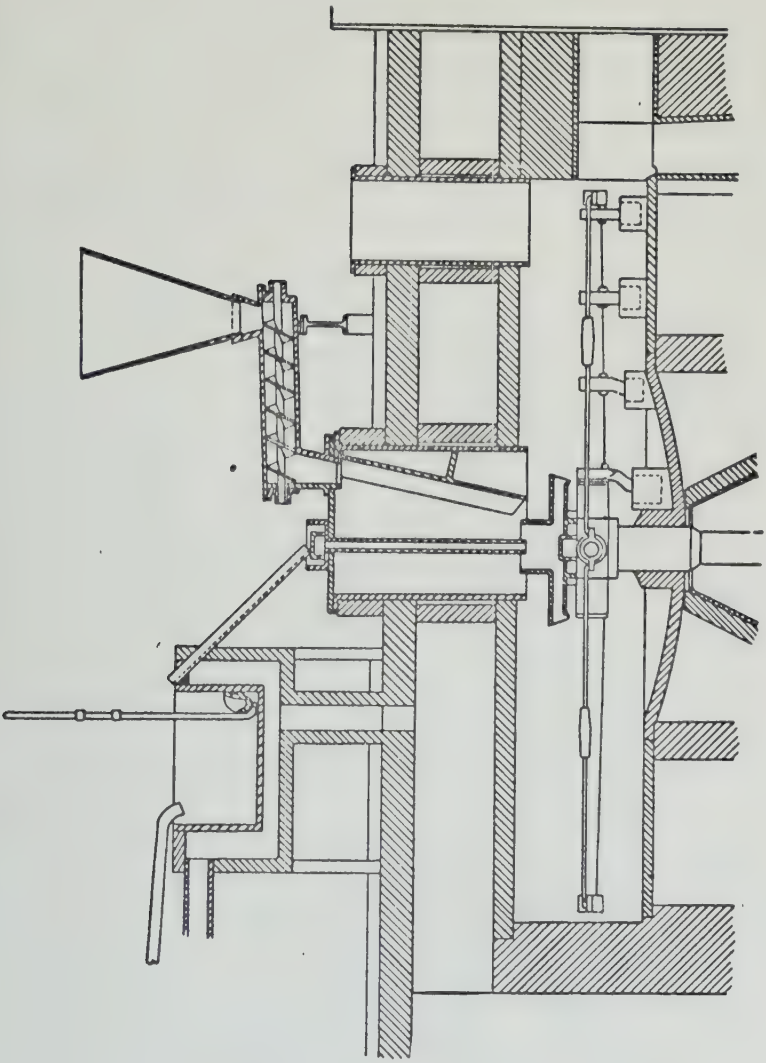

FIGURE 9.—Krickbaum's furnace with Guhlman and Grasselli's feed for molten nitre cake. Vertical section.

charge can be fed by gravity into the central charging pipe. There is a gas line from this mixer leading into the main gas exit flue from the furnace. Krickbaum's furnace has a fire brick muffle with a bottom formed of a large cast-iron plate, the central part of which contains a saucer-shaped depression where the ingredients of the charge get well mixed when one of them is introduced in the liquid form. There is also a distributor fixed to the top of the shaft by which the incoming acid is uniformly spread about the center of the furnace. Both of these features are illustrated in Figure 9.

A comparatively recent development in this furnace is the perfection of methods of charging the bisulfate in molten form by Guhlman [14] and Grasselli [15] and also by Trevoux.[16] The first two cover the same process and apparatus which is also illustrated in Figure 9. The bisulfate is run from a larger heated reservoir or "soup-pot" to the immediate supply tank. The latter is located on top of the furnace and heated by waste heat from the flue as shown. A mechanical dipper moves up and down in the tank, delivering a measured quantity to the trough that leads into the small central charging pipe and thence to the distributor located on top of the central shaft. This greatly assists intimate mixing and speed of decomposition at low temperature.

Dietz and Latten of Leverkusen also have a form of rotating distributor attached to the main shaft.

Furnaces in which the muffles are made entirely of fire tile or chamotte or ceramic material have been in use for some time. These, of course, are heat-resisting and the charge can be more thoroughly and quickly cooked out than in a cast iron pan. Bezanson and Maxim [17] have patented such a furnace (Fig. 10), another is built by the General Ceramics Company according to the design of Dr. Zieren, and the firm of Zahn & Co., Ltd., of Berlin also builds one according to its own design.

Tufts [18] has patented a furnace consisting of two superimposed

[14] U. S. Pat. 1,370,309.
[15] U. S. Pat. 1,495,555.
[16] U. S. Pat. 1,484,587.
[17] U. S. Pat. 1,544,798.
[18] U. S. Pats. 930,441 and 930,442.

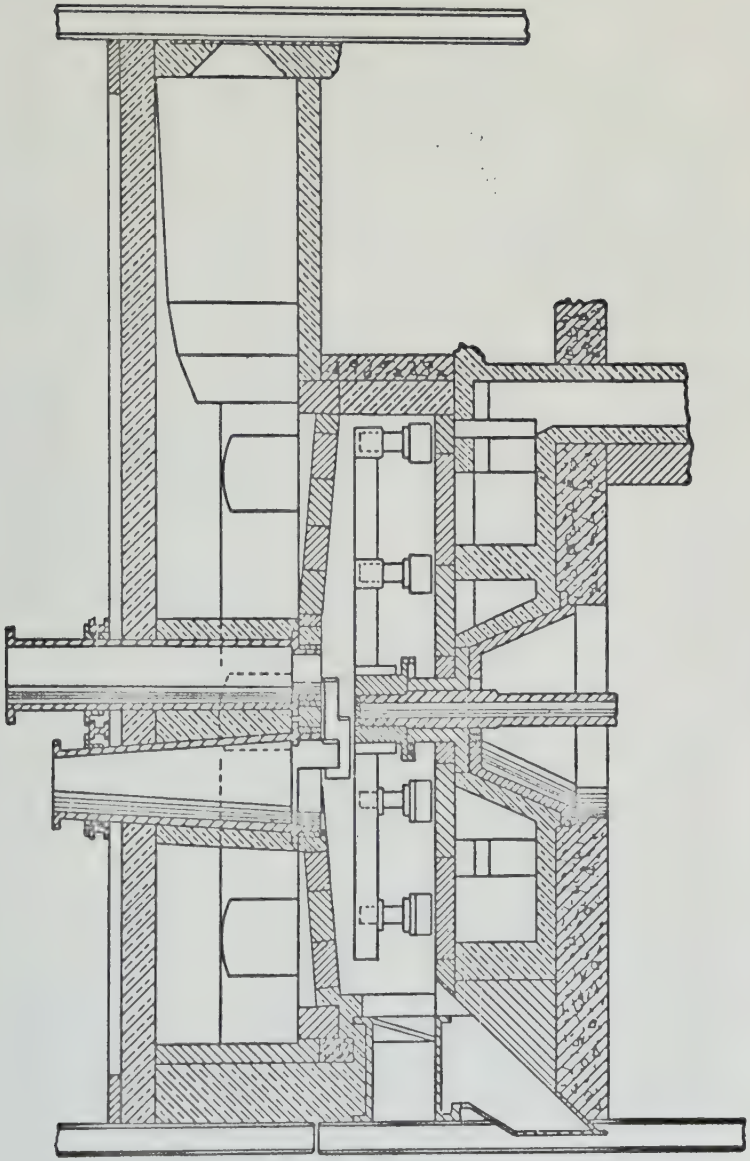

FIGURE 10.—Bezanson and Maxim's fire tile muffle furnace. Vertical section.

circular mechanical muffles with both sets of rakes carried by the central shaft. Its construction is illustrated in Figure 11.

The Modern Rotary Furnace

In 1920 the author built an internally fired rotary furnace with a capacity of a ton of salt cake per hour, operating on nitre cake and salt. Since then several of the same type have been installed because the advantages in the original internally-fired rotary first built by Walker in 1887 have been realized, while the difficulties which defeated his attempt have been circumvented by the application of improved absorption equipment and modern mechanical appliances and methods of firing.

In Figure 12 is shown a plan and elevation of the furnace. It consists of a combustion chamber with oil-burning equipment and a horizontal two-chambered revolving cylinder.

The combustion chamber is lined with fire brick and mounted on a truck for convenience in moving to reach the interior of the furnace. It is made of half-inch steel shell 10 feet long and 4 feet 8 inches in diameter. The combustion chamber nozzle, which projects slightly into the furnace, is a plain iron casting lined with fire brick. The oil burner is the low-pressure type. It is supplied with air by a Sturtevant blower and with oil by Goulds pumps. The air and oil connections are flexible to permit the fore and aft movement of the combustion chamber. There is a course of SiloCel brick between the shell and the fire brick lining. This fully protects the shell and saves heat.

The furnace is a steel shell in two sections of different diameters, united in the middle by cast-steel flanges. The front or hot section has a 9-inch fire brick lining. Its diameter inside this lining is 4½ feet and its length 10 feet. It has a plain unlined cast-iron head with a central port 2 inches greater in diameter than the combustion chamber nozzle, to permit discharge of the salt cake. The latter is also bevelled toward the bottom to give more room for the discharge. A casing is loosely fitted around this end of the furnace through which the salt cake drops to a conveyor. A fan is connected to the top of this casing to conduct the smoke from the hot salt cake to the stack. At the junction of the two sections of

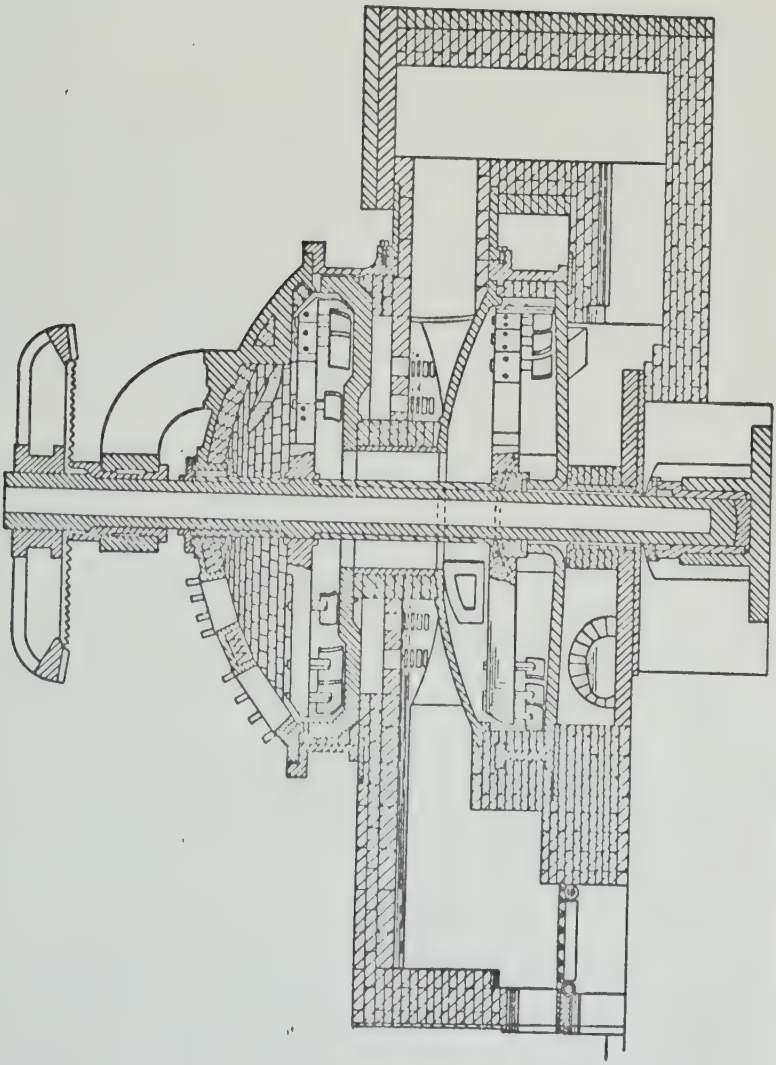

FIGURE 11.—Tuft's superimposed mechanical pot-and-muffle furnace. Vertical section.

the furnace and dividing them into separate chambers there is a cast-iron plate which is bolted to the cast-steel flanges. This plate has a 2-foot hole in the center for the gas and radial slots near the periphery through which the salt cake passes from the grinding chamber to the hot chamber.

The grinding chamber is lined with chilled iron plates. It is 12 feet long and 4½ feet in diameter. It has a cast-iron head which also has a chilled iron lining. An 18-inch cast-iron flue conducts

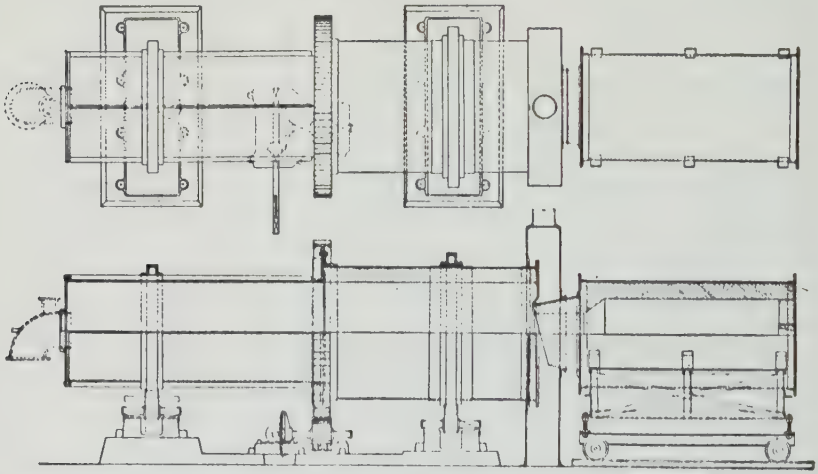

FIGURE 12.—Laury's internally oil-fired rotary furnace. Plan and elevation.

the gas from the grinding chamber to the dust chamber. The charging of the salt and nitre cake is also done through this flue.

The large gear on the furnace is driven by a pinion and chain and a 50 horsepower motor. After the first few revolutions at starting a little less than 25 horsepower is all that is required. The furnace rotates at 16 revolutions per minute.

The normal rate of running is 1 ton of salt cake an hour. This requires 9 to 10 gallons of fuel oil. The burner is easily regulated so that a sootless gas enters the furnace. The heat is regulated according to the quality of the cake. Prime cake has to come out of the furnace at somewhat above 1,000° F. The nitre cake is coarsely ground in a single roll coal crusher weighed in a buggy, the required weight of salt shoveled on top of it and the charge

slowly dumped into the elevator. This is done every 4 or 5 minutes according to the size of charge handled. It is thoroughly ground in the grinding chamber of the furnace and also has given off 25 per cent of its hydrochloric acid when it reaches the hot chamber.

To keep the crust of cake on the brick lining of the hot chamber at the right thickness a loose rail 9 feet long is kept in it. If two or three heavy rails are used, the crust is all cut away, but if only a light one or none at all is used the crust gets too thick. The outside of the furnace is always cool enough to bear the hand.

If there is any interruption of the feed, the fire must be shut off or the charge will fuse on the middle plate and close up the ports. The combustion chamber then must be pushed back and the ports opened with long bars. The operators soon learn to avoid this troublesome job.

The gas leaves the furnace at 300° F., which is close to the minimum that prevents condensation in the grinding chamber, iron flue and dust chamber and represents the best fuel economy possible in the apparatus.

Owing to the thorough mixing in the front chamber and the direct application of the heat in the hot chamber the product runs uniformly under one per cent in both salt and acid. The cake does not lump up on cooling, but remains fine as when it issued from the furnace, only 10 per cent is larger than ten mesh while 43 per cent of it is under sixty mesh. The gas from the furnace has a volume of about 1,000 cubic feet and contains approximately 5 per cent hydrochloric acid. This is absorbed almost completely to form acid of commercial strength and purity as will be shown in the chapter on absorption.

Chapter VI

Salt Cake by Other Methods

Hargreaves Process

Patented in 1870, and only recently given up in England, its first and last home, this process has been so important and is still so interesting as to merit a brief description. It involves the decomposition of sodium chloride by sulfur dioxide and steam and air, thus:

$$2NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2HCl$$

Sulfur dioxide and air in the form of burner gas from a furnace, in which sulfur or sulfide ore are burned, are made to pass through the salt in prepared lumps resting on perforated false bottoms in a series of eight vertical steel chambers 18 feet in diameter by 12 feet high (Fig. 13). The flues are so arranged that by means of dampers the hot gas is first let into the particular chamber where the conversion of the salt is nearly completed and then is directed into the remaining chambers following the order of their degree of conversion, finally passing through a freshly charged chamber where the large excess of undecomposed salt finishes the conversion of sulfur dioxide to hydrogen chloride. This chamber gas is then conducted to an absorbing system and made into hydrochloric acid. One of the chambers is always cut out of the circuit to remove finished sulfate and to recharge. The cycle for each chamber lasts three days. The reaction is exothermic but to carry it to completion some coal, amounting to 250 pounds per ton of salt cake, must be fired on the grates shown in the side walls in the figure. Very good salt cake and acid were made by this method but it could not survive the necessity for the large amount of hand labor involved in its operation.

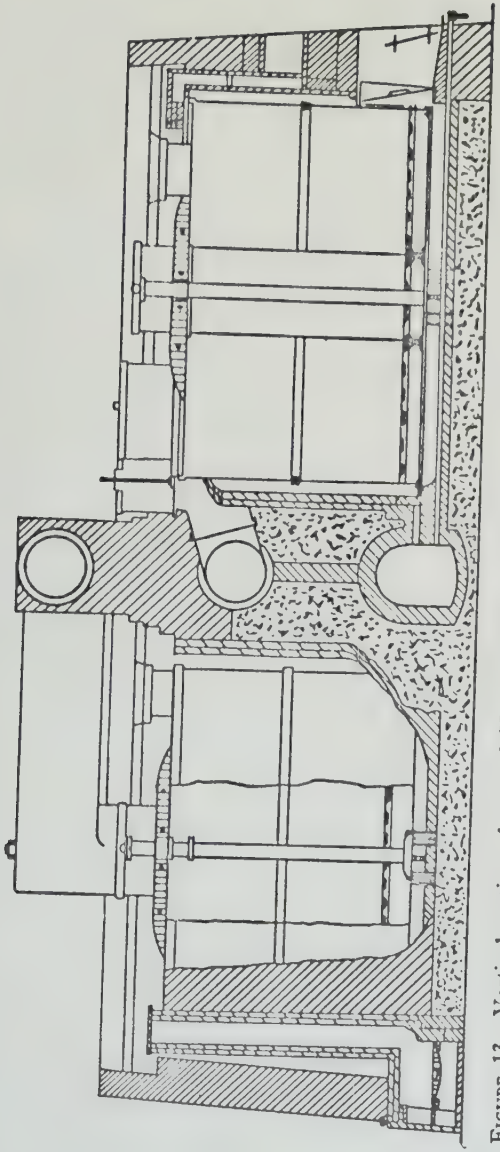

FIGURE 13.—Vertical section of two of Hargreave's reaction chambers, showing false bottoms, gas flues and lateral heating grates.

Weber [1] very reasonably proposes to remove the latter objection to the Hargreaves process by working this reaction in an apparatus of the blast furnace type. The salt, previously prepared in lumps or briquet form, is charged into the mouth of the shaft while the burner gas and steam are forced through the tuyères. The sodium sulfate is removed through the bottom of the shaft, suitable closures being provided at both the top and bottom so that the gas mixture issuing from the furnace can be conducted through a pipe running from the side near the top to an absorbing system. Only a plant scale trial can tell if there are any insuperable difficulties in the application of this idea.

Basset [2] proposes to vaporize sodium chloride and to act on the vapor with sulfur dioxide and oxygen.

Other Methods

Various other methods have been proposed but the only other one which is used commercially is that of decomposing nitre cake with sawdust in direct oil-fired furnaces of the hand-worked reverberatory type or in the rotary. Loeffler [3] claims that the mass is more easily calcinable if the sawdust and molten nitre cake are first mixed and allowed to cool; a porosity of the mass is produced by gasification during setting which renders calcination easier. This may be advantageous in a hand-worked furnace but would not be important in a rotary.

Starke [4] uses sulfur instead of sawdust in the latter process.

Barbier [5] separates Glauber's salt from nitre cake solution by refrigeration.

Meurer [6] makes a mixture from which sodium sulfate can be leached by heating sulfide ore with polysulfide of sodium and sodium chloride.

Pemperton [7] separates sodium sulfate from a solution of mixed

[1] U. S. Pat. 1,500,289.
[2] U. S. Pat. 1,279,499.
[3] U. S. Pat. 1,104,913.
[4] U. S. Pat. 542,429.
[5] U. S. Pat. 484,546.
[6] U. S. Pat. 650,980.
[7] U. S. Pat. 685,792.

salts by boiling to throw out anhydrous sodium sulfate. This is intended for use on natural deposits containing the salt as is also Hoepfner's [8] method of running a solution of mixed salts into a sodium chloride solution cooled to — 10° C.

Gilman [9] dissolves zinc in a nitre cake solution for use in precipitating out lithopone with barium sulfide and then recovers the sodium sulfate from the filtrate.

Pennock [10] obtains sodium sulfate by neutralizing nitre cake with "fished salts" from alkali works.

Other methods of converting nitre cake into sodium sulfate have been patented: Hart [11] cools a nitre cake solution to — 10° C.; Kee [12] heats nitre cake to drive off sulfur trioxide; Nibelius [13] extracts the acid from a solution of nitre cake with alcohol; and Holmes [14] washes out the acid from nitre cake by extraction with water counter-current.

The method of decomposing lead sulfate with sodium carbonate was patented by Ramage.[15]

[8] U. S. Pat. 704,036.
[9] U. S. Pats. 732,732 and 770,963.
[10] U. S. Pats. 870,746 and 922,031.
[11] U. S. Pat. 1,313,192.
[12] U. S. Pat. 873,078.
[13] U. S. Pat. 1,354,649.
[14] U. S. Pat. 871,066.
[15] U. S. Pat. 1,258,985.

Chapter VII

Hydrochloric Acid Produced from Chlorine and Hydrogen, and Other Methods

Action of Light on Chlorine and Hydrogen

Chlorine and hydrogen unite in equal volumes to form hydrogen chloride; the heat of formation is 22,000 calories. The gases do not combine in the dark, but light induces reaction, the rate of which increases with the intensity of the light. Candle, gas and oil flames cause slow reaction; sunlight or lime-light cause explosion. If the gases are dried they do not explode in the sunlight. They are exploded moist or dry by an electric spark. Excess of either gas increases the velocity of the explosion wave. The gases ignite when heated to about 200° C. in a closed vessel and at 430° to 440° at atmospheric pressure. With moist gases this may be as low as 260°. Catalysts induce reaction; platinum black or charcoal cause explosion even in the dark. The presence of oxygen decreases the velocity of the reaction. Chlorine molecules excited either by light in the visible portion of the spectrum or by thermal collision do not dissociate into atoms except on collision with water molecules.[1]

The Actinometer.[2]—The measurement of the intensity of actinic rays is based upon the chemical transformation which they can effect. The hydrogen-chlorine actinometer utilizes the discovery in 1809 by Gay-Lussac and Thenard that light has a marked influence on the union of these two gases. Draper[3] constructed an actinometer in which these two gases were used, but this was greatly improved by Bunsen and Roscoe,[4] whose work in this field was of fundamental importance. Their apparatus is shown in Figure 14. The glass tube is filled with a mixture of equal parts of hydrogen and chlorine, obtained by electrolyzing a solution of hydrochloric acid of specific gravity 1.148, using carbon electrodes. The lower

[1] Lewis & Rideal, *J. Am. Chem. Soc.* **48**, 2553 (1926).
[2] Jones, *Elements of Physical Chemistry* (1915).
[3] *Phil. Mag.* (3) **23**, 401 (1843).
[4] *Pogg. Ann.* **100**, 43 (1857); **101**, 235 (1857); **108**, 193 (1859).

blackened portion of i contains water. This is connected at one end with a tube closed by a stopcock, h, and at the other with a tube, k, which is connected with a vessel, l, filled with water. After the liquids have become saturated with the mixture of gases, h is closed, and the whole tube protected from the light except the bulb i. The light is now allowed to fall on this bulb, when some of the

FIGURE 14.—The actinometer.

gases combine, forming hydrochloric acid. The latter is absorbed by the water in i, and the column of water moves from l along the graduated tube k. By this means the amount of gases which have combined is readily determined, and from this the intensity of the photochemical action. If the light is too strong, explosions may result in this form of actinometer.

SOURCES OF CHLORINE AND HYDROGEN

Plants for the commercial production of hydrochloric acid from chlorine and hydrogen are in operation in this country, in Canada and in Europe. Chlorine and hydrogen are by-products of the electrolytic caustic soda process, in which they are produced in molecular equivalent quantities. The hydrogen is in pure form and may be used for hydrogenation, for production of synthetic ammonia or for other purposes, but it is generally allowed to escape, while the chlorine is made into bleach or liquefied. The caustic soda is always in greater demand than the equivalent chlorine and the disposal of the latter has been such a problem as to give birth a few years ago to the Chlorine Institute, Inc., which is devoted exclusively to the relief of the chlorine industry. A chlorine symposium was the feature of the Chicago meeting of the American Electrochemical Society in 1926; its object was to consider methods of increasing the use of chlorine. These and other similar movements have encouraged the use of electrolytic chlorine for making hydrochloric acid. The manufacture of hydrochloric acid from these gases has thus received a great deal of attention and several efficient processes have been developed. The product is of superior quality and thus has a sales advantage, but the quantity manufactured is

relatively small and the conclusion is, therefore, that chlorine still costs too much to permit extensive competition with hydrochloric acid made from salt and sulfuric acid. A possible extensive development of our large natural sodium sulfate deposits with its consequent influence on the output of hydrochloric acid from salt and sulfuric acid may eventually change this situation but, for some time to come, it is not probable that electrolytic hydrochloric acid will figure largely in the acid market.

In the commercial processes which have been developed, the hydrogen for the reaction may come from two sources: the first is the use of the hydrogen simultaneously produced during electrolysis, and the second is the cheap source of hydrogen which is afforded when steam comes in contact with highly heated carbon.

Chlorine and Electrolytic Hydrogen

If the hydrochloric acid and the chlorine are made in the same plant the hydrogen generated by the cells is of course used. The process of greatest interest, because its product is so well known, is that of the Hooker Electrochemical Company of Niagara Falls. According to the patent of their assignee, Townsend,[5] chlorine is caused to combine with hydrogen in a closed system, confining such an excess of hydrogen that a product results which is entirely free from uncombined chlorine. The means by which this is contrived is illustrated in the diagram, Figure 15. The excess of hydrogen required is maintained by a gasometer (25) connected in the cycle. The constant quantity reacting with the chlorine joins the main stream through special valve (15) all passing through drier (14) and joining the entering chlorine at the mixing chamber (10), the chlorine having been admitted at (11) and dried at (12). The mixture then burns in chamber (16), which is merely a refractory tube; the resulting hydrogen chloride and hydrogen mixture is then passed through the water-cooled pipes (17), entering the absorbing tower (18) through pipe (19). Here the hydrogen chloride is absorbed by water entering through trap (23), passing through distributor (20), and collecting in a reservoir (21), from which the acid overflows at (22), the excess hydrogen returning to the

[5] U. S. Pat. 1,414,762.

gasometer through (24). Now in order to keep the stream of hydrogen in motion a part of the water is admitted at (31), passing through (30), which is a form of ejector where the suction caused by the stream of water draws in hydrogen through pipe (32). After passing through pipe (29), both enter the separator (26), which the gas leaves under a slight pressure through pipe (28), while the water flows to the tower through trap (27).

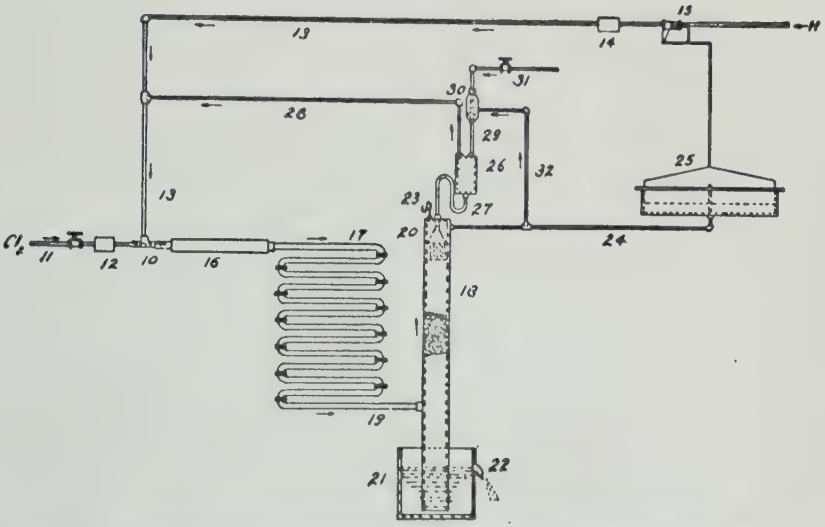

FIGURE 15.—Diagrammatic illustration of Townsend's process using hydrogen and chlorine.

Moore [6] has described the Brown Co.'s plant at Berlin, N. H. In this paper he also gives a chronology summarizing the industrial development of chlorine, especially with reference to hydrochloric acid, from 1772, when Priestly first collected gaseous hydrogen chloride over mercury, to 1922, when Townsend's patent was issued. The principal features of Moore's process are a furnace consisting of an iron box lined with fire brick set in china clay. The furnace is started by placing an oil-soaked piece of waste on the floor through a hole in the top, igniting it and supporting the combustion with hydrogen until it is quite hot; the top hole is then plugged and the chlorine turned on. There is a safety seal in the entering gas

[6] *Trans. Am. Inst. Chem. Eng.* **14**, 91-123 (1923).

line near the furnace which is made of a light sheet iron can placed like a gasometer bell, so that it can easily be blown out when there is an explosion.

The inlet and outlet pipes of the furnace are made of fused silica, and the temperature must be kept below 1,200° C. to preserve them. This is done by the air entering with the chlorine; there is ample dilution with air because the chlorine side of the cells is always under a slight vacuum. The hydrogen side is kept at a pressure of one inch of water.

These typical conditions are given:

Composition of gas (per cent)	
Chlorine entering furnace	4
Hydrogen leaving furnace	0
Temperatures (° F.)	
Hydrogen entering furnace	63
Chlorine entering furnace	55
Atmosphere of furnace	1,470
Gas entering air-cooled gas cooler	680
Gas leaving air-cooled gas cooler	370
Gas entering water-cooled gas cooler	130
Theoretical production, pounds HCl per day	121

The absorbing system is typical, having an air-cooled gas cooler made of fused silica "S" pipes, a water-cooled gas cooler consisting of a submerged stoneware coil, a series of submerged Cellarius absorbers and a coke-packed stoneware terminal tower.

These essential factors are mentioned for most successful operation:

1—Continuous running.
2—Maintaining hydrogen supply under a light pressure to exclude air leaks.
3—Use of strong chlorine gas with large excess of hydrogen to keep down operating temperature.
4—Extreme care in starting the system.
5—Plenty of cooling water.

Roberts [7] in his patent of 1905 claimed a process of producing hydrochloric acid by generating hydrogen and chlorine in a cell, conducting each gas in a separate stream to a common point, causing

[7] U. S. Pat. 807,640.

the gas streams to impinge directly on each other at such point, and burning the gases at the point of impingement.

In the Gibbs [8] process hydrogen is also used in excess but the gases are separately heated to ignition point before mixing.

Englestad [9] starts the combustion with electric spark plugs.

Scherbel [10] has patented a refractory chamber with a special arrangement of nozzles for burning hydrogen and chlorine.

In the process of the Badische Anilin-und-Soda-Fabrik,[11] an igniting safety flame is provided at the junction of the streams of entering gases which is so arranged as to cause the combustion to take place in a downward direction. The main gas supply is controlled in order to give equimolecular proportions of hydrogen and chlorine. Cooling is provided for the walls of the shaft furnace in which the combustion is carried on. The main supply of gas enters through pipes in the top of the furnace; between these are the small pipes through which gas enters to support the igniting flame. To effect complete combustion, the reaction gases are passed, preferably after partial cooling, through contact material placed at the lower end of the furnace and consisting of brick, pumice or quartz coated with metal salts.

With regard to the influence of oxygen on the reaction, Neumann [12] says that the combustion of equivalent quantities of hydrogen and chlorine or combustion with excess of the former produces only chlorine-free hydrogen chloride. By introducing air, or using gases containing air, chlorine-free hydrogen chloride is also obtained if the quantity of hydrogen suffices for both the chlorine and the oxygen. If there is insufficient hydrogen, chlorine is found in the gas. Under possible temperature conditions of "chlorine burning," the quantity of chlorine can at most be only a few per cent of the hydrogen chloride gas.

D. A. Pritchard [13] reports that the light of a mercury arc lamp

[8] U. S. Pat. 779,998.
[9] U. S. Pat. 1,121,910.
[10] U. S. Pat. 1,184,576.
[11] Brit. Pat. 173,300 of 1922.
[12] *Z. angew. Chem.* **36**, 529.
[13] *Chem. & Met. Eng.* **33**, 275.

has been found to be entirely satisfactory in the synthetic hydrochloric acid plant of the Canadian Salt Co., in Windsor, Ont.

Chlorine and Water Gas

The most economical way of conducting the commercial application of the reaction between chlorine and hydrogen when the latter is generated by the contact of steam with incandescent carbon is to pass the chlorine together with the steam over the carbon. Thus the endothermic reaction between water and carbon is supported by the exothermic reaction between hydrogen and chlorine. The various processes for using hydrogen so generated are all conducted in this manner and they differ from each other only in detail.

Gamer and Clayton [14] have a method of control of the reaction in a chamber containing wood charcoal heated to 340° C. from the outside. The gases are admitted with a little moisture and the hydrogen taken in excess; the excess is returned to the system after the absorption of the hydrogen chloride.

Peter [15] passes a mixture of chlorine and steam into a chamber containing charcoal or coke heated from the outside. If the vapors are taken in the ratio of seven parts of water to three parts of chlorine, complete conversion at 200° C. is claimed. Gibbs [16] found that this temperature may be as low as 130° C. if activated carbon is used.

Paulus [17] passes chlorine, steam and air through a previously ignited column of coke in such proportions that no external heat is required. The gases having been cooled and the hydrogen chloride absorbed as shown in Figure 16 the exit consists of a mixture of nitrogen and carbon monoxide of 99 per cent purity.

Rosenstein,[18] with practically the same equipment, varies the amount of water so as to produce carbon dioxide.

The process of the Great Western Electrochemical Company, described by Hirschkind,[19] also uses water in the proportion to form carbon dioxide in the exit gas. Apparatus similar to that of Paulus

[14] U. S. Pat. 1,220,411.
[15] U. S. Pat. 1,229,509.
[16] *Ind. Eng. Chem.* 12, 538 (1920).
[17] U. S. Pat. 1,420,209.
[18] U. S. Pat. 1,485,816.
[19] *Ind. Eng. Chem.* 17, 1071 (1925).

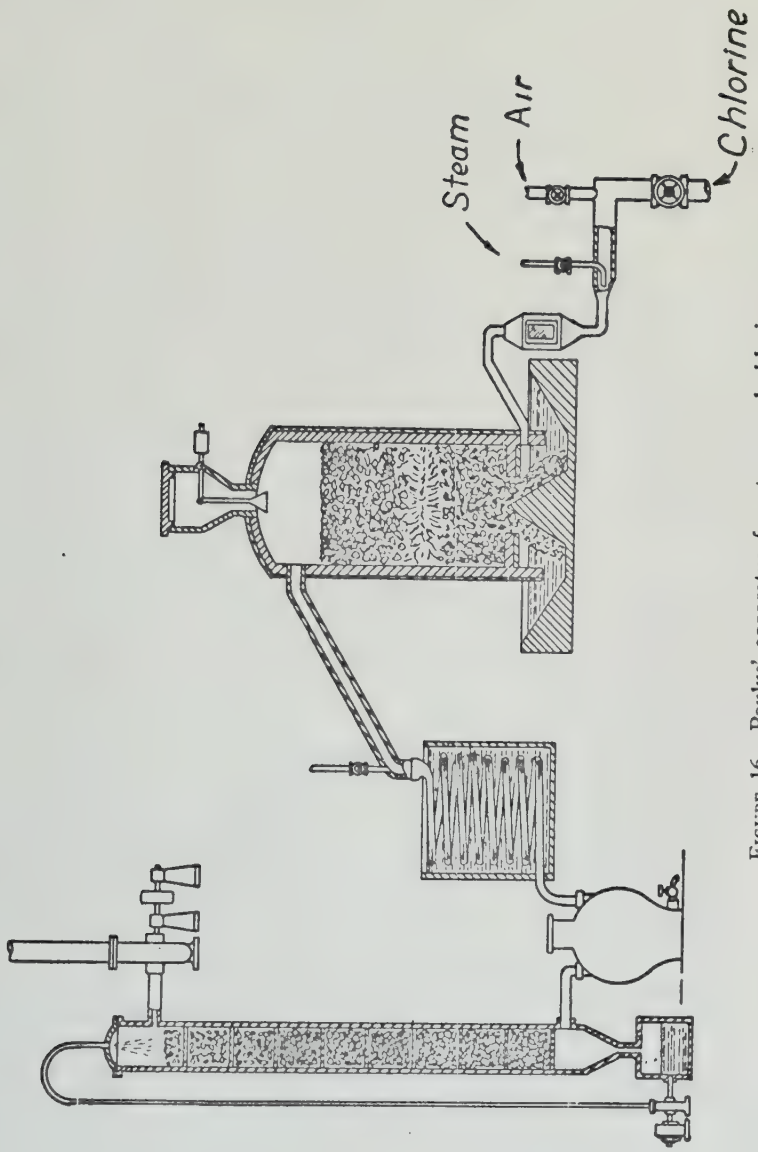

FIGURE 16.—Paulus' apparatus for steam and chlorine.

is employed with the addition of a dust chamber next to the furnace and a set of absorption tourills between the gas cooler and the absorbing tower. With 80 to 85 per cent chlorine gas a concentration of 60 to 70 per cent hydrogen chloride can be maintained at the furnace outlet. There is practically no condensation in the gas coolers. Excess steam for carrying off the heat of the reaction is unnecessary and undesirable. If the entering gases are proportioned according to equation,

$$C + 2Cl_2 + 2H_2O = 4HCl + CO_2$$

the furnace can be run steadily with a temperature outlet of 900° C. and with an outlet gas mixture containing almost all of its carbon and oxygen in the form of carbon dioxide and with no chlorine or only a trace.

Westhausser [20] has patented a process for making hydrochloric acid from hydrogen and chlorine by reaction with basic zinc chloride with subsequent hydrolysis, thus:

$$ZnCl(OH) + Cl + H = ZnCl_2 + H_2O$$
$$ZnCl(OH) + H_2O = Zn(OH)_2 + HCl$$
$$ZnCl_2 + H_2O = Zn(OH)_2 + HCl$$

Everette [21] proposes to make hydrogen chloride by subjecting a mixture of air, water and chlorine to contact with incandescent silica.

Acid from Organic Chlorinations

In chlorinating organic compounds the substituted hydrogen combines with chlorine to form hydrogen chloride. The quantity of this that could be recovered as by-product hydrochloric acid is probably considerable in the aggregate but coming from scattered sources and in plants of concerns not already in the business of marketing the acid, it does not seem to have any future whatever except for local plant consumption. Aylsworth [22] has patented a process of chlorinating naphthalene under pressure and absorbing the hydrogen chloride simultaneously produced. Such modifications as can be made in the method of conducting these organic reactions so as to recover hydrochloric acid should never involve a sacrifice in the

[20] U. S. Pat. 791,306.
[21] U. S. Pat. 805,009.
[22] U. S. Pat. 914,223.

yield or quality of the organic product because of the relatively slight value of the by-product acid.

Chlorine and Sulfur Dioxide

Sulfuryl chloride is easily converted to an equivalent mixture of sulfuric and hydrochloric acids by the addition of water,

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

The chloride is a liquid with a very pungent odor but it does not corrode steel and is safely transportable in ordinary acid drums. Professor Ralph McKee [23] has suggested it as a convenient, highly concentrated source of sulfuric and hydrochloric acids for shipment to distant points. He has developed processes for the preparation of sulfuryl chloride from chlorine and pure sulfur dioxide as well as from chlorine and sulfur burner gas by contact with activated carbon. In connection with the extension of a liquid sulfur dioxide plant the author has prepared sulfuryl chloride by this method and found that with the dried sulfur dioxide and chlorine gas the reaction is quantitative.

In Melling's process [24] the formation of sulfuryl chloride from sulfur dioxide and chlorine and its decomposition into sulfuric and hydrochloric acids by water are performed in one operation by irradiating a mixture of the gases with mercury-vapor lamps during their passage through a glass vessel, simultaneously spraying them with water. Welsh [25] proposes to separate the gaseous mixture of sulfuric and hydrochloric acids resulting from the reaction between chlorine, sulfur dioxide and water vapor, by electrical precipitation of the sulfuric acid.

Other Methods

The decomposition of potassium chloride into hydrochloric acid and a potash salt is carried on to a small extent in this country. If sulfuric acid is used the reacting mass is very corrosive to iron and will rapidly destroy the cast iron vessels generally used for decomposing sodium chloride. Meyer and Klages [26] propose to

[23] *Ind. Eng. Chem.* 16, 279 (1924).
[24] U. S. Pat. 1,430,035.
[25] U. S. Pat. 1,285,856.
[26] U. S. Pat. 1,099,451.

charge the potassium chloride and sulfuric acid into a molten mass of potassium bisulfate in a manner similar to that described on page 63 for sodium chloride. Kersten [27] makes hydrochloric acid from potassium chloride by passing superheated steam through a molten mixture of potassium chloride with potassium silicate. Comment [28] uses direct heat to decompose a mixture of potassium chloride and 60 degrees Baumé sulfuric acid.

Fox and Whittaker of the Bureau of Soils at the 72nd Meeting of the American Chemical Society in Philadelphia, Sept. 5 to 11, 1926, outlined a method whereby hydrochloric acid may be produced as a by-product in the manufacture of potassium sulfate from potassium chloride and sulfuric acid. The hydrochloric acid so produced may be utilized for the digestion of phosphate rock. Dicalcium phosphate is precipitated from the hydrochloric acid solution of phosphate rock, preferably by the addition of milk of lime.

Phosphate rock itself reacts with the phosphate in the solution to form dicalcium phosphate to only a limited extent. The reaction is stopped by the interference of the insoluble dicalcium salt. Calcium carbonate reacts with the phosphates in solution to form a mixture of dicalcium and tricalcium phosphates. Calcium chloride is produced by this method as a by-product.

The present American potash situation, while a vast improvement over that existing prior to the World War, has certain weaknesses, among which is the lack of diversity in the high-grade potash salts produced. High-grade potassium chloride constitutes the bulk of the American output and an even higher percentage of the high-analysis product. Consequently we are still dependent on Europe for the other high-grade salts so essential to many industries.

An interesting reaction of no commercial importance is that of Low,[29]

$$SiCl_4 + 2H_2O = 4HCl + SiO_2$$

and also of Seamon,[30]

$$CaCl_2 + C_2H_2 = CaC_2 + 2HCl.$$

[27] U. S. Pat. 1,533,009.
[28] U. S. Pat. 1,417,887.
[29] U. S. Pat. 1,451,399.
[30] U. S. Pat. 826,614.

The recovery of hydrochloric acid as a by-product in certain metallurgical processes, such as from chloridized metals with steam and air and from nickel-copper matte treatment has been proposed by Mond,[31] Rumpf,[32] and Wells,[33] but it is doubtful if such processes could be made to pay except for the purpose of regenerating acid for re-use in the plant.

Kerr [34] mixes magnesium chloride with nitre cake, heats to drive off hydrogen chloride and then separates the remaining mixture of Epsom and Glauber's salts by crystallization. Galt [35] has patented a method of making hydrochloric acid and gypsum from calcium chloride and sulfuric acid.

[31] U. S. Pat. 379,487.
[32] U. S. Pat. 361,026.
[33] U. S. Pat. 940,293.
[34] U. S. Pat. 1,203,357.
[35] U. S. Pat. 1,581,436.

Chapter VIII

Absorption Principles and Equipment

Hydrogen chloride and water have an intense affinity. In hydrochloric acid containing 20.24 per cent HCl or less the gas is combined in the form of hydrates and cannot be blown out with air. Acid under this strength will absorb all of the hydrogen chloride from air or furnace gases down to insignificant amounts.

In the preparation of strong hydrochloric acid the formation of this solution of hydrates is a distinct step. Absorption systems are so arranged that water enters counter-current to the gas mixture from which the hydrogen chloride is to be completely removed, so that the strong gas meets the acid that is nearly saturated with the hydrates. Above this point the hydrogen chloride is merely held in solution; its vapor pressure rises rapidly with concentration and it can be blown out of the solution with a current of air; accordingly other conditions regulate the preparation of stronger solutions.

The Mechanism of Absorption

Lewis and Whitman [1] have given us a good way to visualize the mechanism of absorption. The gas and the liquid films at the boundary can be indicated as having a definite thickness, although actually no such sharp demarkation exists. Conditions outside of the gas film are the same as in the main body of the gas, while those at the inside of the liquid film are the same as in the main body of the liquid. The gas and the liquid at the boundary between the two films are in equilibrium. Absorption occurs, therefore, through two films in series. The rate of absorption per unit area equals the diffusion coefficient for gas film multiplied by the difference in partial pressure across the gas film and also equals the diffusion

[1] *Chem. & Met. Eng.* 29, 146 (1923).

coefficient for the liquid film multiplied by the difference in concentration across the liquid film.

With water or weak acid, where the partial pressure of hydrogen chloride is negligible, the rate of absorption is determined solely by the rate of diffusion through the gas film, so that the gas is absorbed as rapidly as it can reach the surface of the liquid. With high concentrations of acid, however, the absorption of a small amount of acid into the surface brings the surface into substantial equilibrium with the gas, thereby preventing absorption until the absorbed hydrogen chloride has diffused through the liquid film into the interior.

Absorption systems are designed to make 18-, 20- and sometimes 22-degree Baumé acid and the gas concentrations of interest are therefore the minimum hydrogen chloride volume per cent which will make this acid at the usual temperature extremes.

Walker [2] showed that the vapor pressure of a solution can be determined by passing a measured volume of air through it and then measuring the amount of vapor of the solution carried by the air. The reverse of this operation must therefore answer the question. For his purpose Walker states the gas law, thus,

$$p = \frac{g}{Mv_1} RT$$

Table 18 is calculated from this equation, using vapor pressures in Table 10 and solubilities in Table 1. These considerations emphasize the three principal conditions that control absorption, namely, (*a*) motion of absorbent and gas, (*b*) gas concentration, (*c*) temperature.

TABLE 18.—*Minimum gas concentrations required to make 18-, 20- and 22-degree Baumé acid.*

Temperature, ° C.	*HCl, per cent by volume*		
	18° Bé.	20° Bé.	22° Bé.
0	0.098	0.46	2.24
10	0.23	1.51	4.41
20	0.47	1.94	8.23
30	0.94	3.69	14.46
40	1.85	6.80	25.59

[2] *Z. physik. Chem.* **2**, 602 (1888).

The current use of packed towers provides ample motion of gas and liquid at the interface to prevent equilibrium and thus permits the maximum rate of absorption per unit area. For unit volume, efficiency is highest with coke packing or similar cellular material. Gas concentrations for the production of 18- and 20-degree Baumé acid are always higher, in any type of furnace, than the minimums shown in the table. The influence of temperature is considerable, hence unit volume efficiency is greatly increased by cooling.

Using Thomsen's equation,

$$[HCl(m+1)H_2O] = \frac{m}{m+1} \cdot 11980 + 5375 \text{ calories},$$

where m is the number of gram mols of hydrogen chloride, Cumming [3] calculates that the heat evolution when 1 gram of hydrogen chloride is dissolved in sufficient water to give a 30 per cent solution is about 400 calories.

He further calculates that the total heat in the furnace gas corresponding to 1 gram hydrogen chloride, when using 60 degree Baumé sulfuric acid and making moderate allowance for dampness in the salt and moisture from the combustion of fuel, a total allowance of 0.70 gram of water per gram of hydrogen chloride, to be as follows:

Cooling 0.70 g. of steam from 500° to 100°	about	140	calories
Cooling 0.70 g. of water from steam to liquid	"	370	"
Cooling 1.00 g. of HCl from 500° to 100°	"	70	"
Solution of 1 g. of HCl to give 30% solution (extra water added cold)	"	400	"
Cooling 3 g. of solution from 100° to 30°	"	270	"
Total heat change	"	1250	"

No account is taken here of the diluting air but he states that this is never likely to be below 25 per cent of the total cooling required, and may with very dilute gases run up to over 90 per cent of the total.

Gas-cooling Equipment

By far the most satisfactory apparatus for cooling the furnace gas before absorption is a cooler made up of fused quartz *S*-pipes

[3] Lunge & Cumming, *Manufacture of Acids and Alkalies*, vol. 5, p. 238.

over which water may be distributed. This material is very fragile but, unlike stoneware, it is never broken by heat changes and once in place and well supported it lasts a long time. These coolers are shown in Figures 17 and 18. The usual size of an *S*-pipe is 6 feet 6 inches from center to center of the bends and 6 inches inside diameter. They are usually set in parallel rows of eight or ten pipes each. The number of pipes for a given job may be calculated by this formula,

$$Q = \frac{Ft}{\frac{1}{x_1} + \frac{1}{x_2} + \frac{d}{N}}$$

in which

Q = Heat removed per hour in kilogram calories
F = Area of surface in square meters
t = Difference in temperature
a = Thickness of wall of pipe in meters
N = Coefficient of thermal conductivity (0.1 for fused silica)
x = Coefficient of conductance of films
x_1 = Coefficient of conductance water to pipe, boiling liquids = 10,000
x_2 = Coefficient of conductance between gas and pipe = 8,000.

Examples from operating plants:

Plant No. 1 has 6 rows of 8 *S*-pipes [4] taking 1000 cubic feet per minute of gas containing 5 per cent hydrogen chloride from a direct oil-fired rotary. The temperature of the gas at the cooler inlet is 130° F. in winter and 170° F. in summer and at the outlet it is 60° F. and 90° F. respectively. The cooling water on is 42° F. and off 58° F. in winter for a volume of 15 gallons per minute. The velocity of the gas in the pipes is about 14 feet per second and the cooling rate 1.4° F. per linear foot of pipe in winter and 1.3° F. in summer.

Plant No. 2 has 4 rows of 7 *S*-pipes [5] taking 340 cubic feet per minute of gas from a pot and muffle furnace which varies from 5 to 30 per cent hydrogen chloride during each charge. The temperature at the cooler inlet is 310° F.; at the outlet, without any cooling water, it is 98° F. and with 10 gallons per minute of water it is 75° F. This cooling water is 40° F. going on and 58° F. going

[4] General Ceramics Co. Fused Silica.
[5] Thermal Syndicate, Vitreosil.

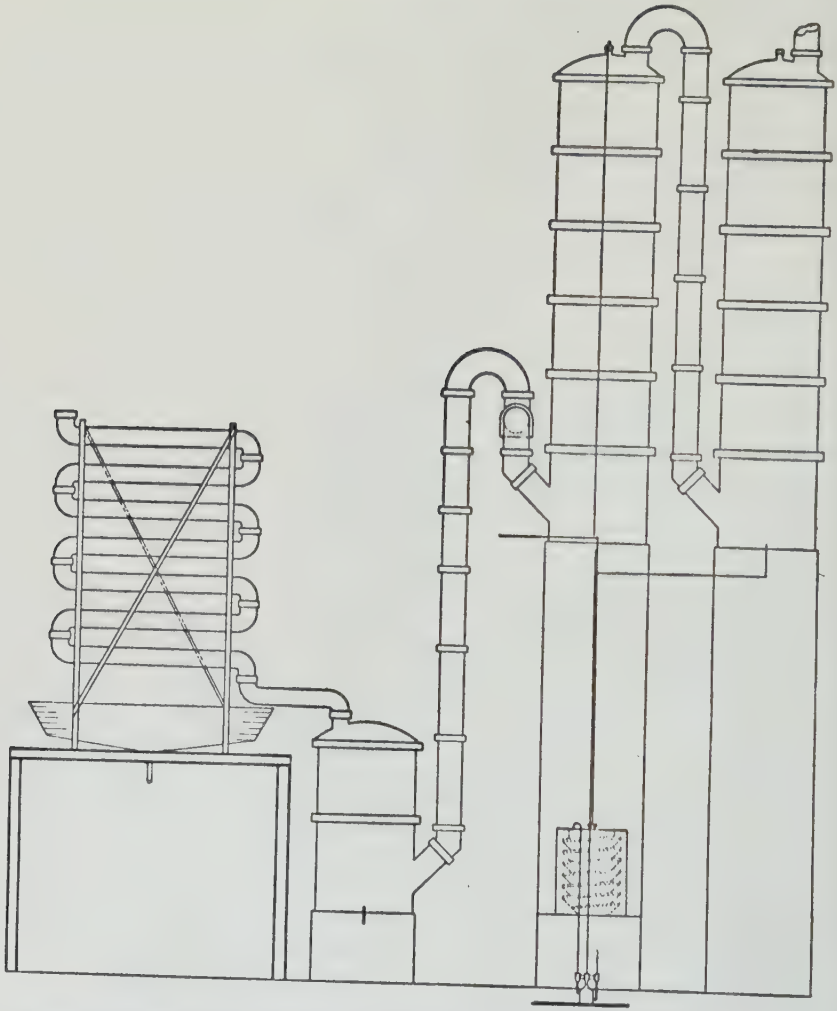

FIGURE 17.—Absorption system for concentrated gases, showing gas cooler, coke filters, absorbing towers, absorbing acid cooling coil and pulsometers.

off. The gas velocity is only 4 feet per second in the pipes and cooling rate is 4.3° F. per linear foot without water and 5° F. with water.

The best grades of chemical stoneware pipe do not crack but serve very well with warm gas, especially where there is no water

cooling; that is, all lines beyond the fused silica gas cooler can safely be made of this material for pot-and-muffle furnaces where the gases vary considerably in temperature within the period of a charge. All lines on the furnaces and retorts delivering gas of uniform temperature and composition may safely be made of it wherever the gas temperature is under 212° F. Wherever chemical stoneware can be used, it is preferable to fused silica because this

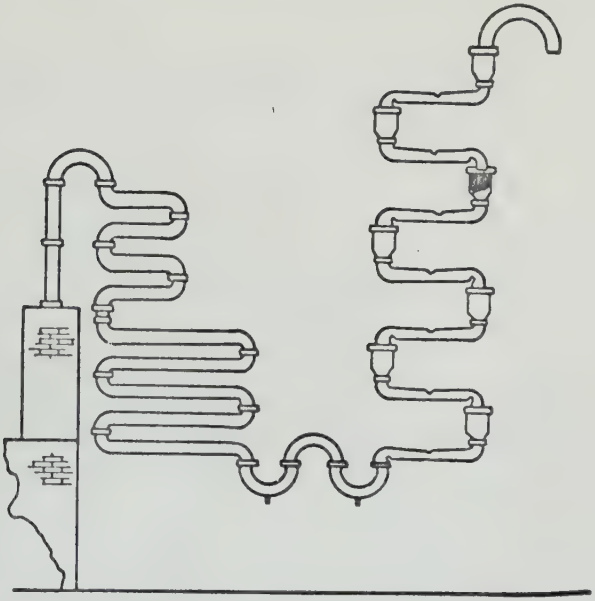

FIGURE 18.—Absorbing system of fused silica showing Vitreosil absorbers.

is safer to handle and cheaper in price and it resists the action of the acid indefinitely.

Under certain circumstances some cooling can be done in cast iron pipes but if there is any condensation at all the iron is quickly dissolved away, therefore, it can only be used at temperatures above the point where sulfuric and hydrochloric acids may condense, which means that it is restricted to a few feet at the furnace outlet.

None of the new acid-resisting iron or other alloys (Table 5) are sufficiently resistant to hot, strong or even cold, weak hydrochloric acid to make them applicable. Apart from the cost of more fre-

quent renewal, they are relatively expensive and would also contaminate the product with iron or other metals.

Cooling Equipment for Absorption Systems

The other point in the process where cooling is necessary and where air-cooling does not always give desired temperatures and water-cooling must be applied is the absorbing system. Here as already mentioned an amount of heat is generated by the reaction

FIGURE 19.—Woulff tourill.

between the gas and the water which is sufficient to prevent formation of acid of the commercial grades unless there is sufficient air or water-cooling or both. In many cases water-cooling of the absorption apparatus may be dispensed with entirely. It was rarely applied on the old pot-and-muffle plants in this country.

If the absorption is conducted in the old type receiver or Woulff tourill (Fig. 19), or in the similar but improved shapes called

Cellarius absorbers (Fig. 20), or in Meyer absorbers (Fig. 21), some of these vessels, usually the first few to receive the gas, are placed in a shallow water-tight wood trough in which they are submerged in water. If it is desired to produce 22-degree Baumé acid, especially in hot weather, it is advisable to water-cool about twenty-five per cent of the absorbers in a system in this manner. Thus, a typical absorbing system for a pot-and-muffle furnace making nine tons of 20-degree Baumé acid in twenty-four hours would have two

FIGURE 20.—Cellarius absorber.

rows of thirty of these absorbers, one for the pot side and one for the muffle side, and the first eight on the pot side would be cooled because these receive gas running up to 30 per cent hydrogen chloride and over within the first 40 minutes after charging; during that time the acid in them warms up considerably and only a small amount of 22-degree Baumé acid can be made except in cold weather. If the heat is removed by water-cooling so as to maintain the temperature of the acid under 80° F., then 22-degree Baumé acid can be made during that whole 40 minute period. The advantage of cooling all of the other receivers on both the pot-and-muffle sides is that fewer are required and the plant investment is thus reduced, but it has been the custom to regard the absorbers partly as storage capacity, particularly if they are 85-gallon Woulff tourills [6] in which the saving is to be balanced against the cost of equivalent storage elsewhere.

Another form of water-cooled absorber is shown in Figure 18.

[6] Maurice A. Knight, General Ceramics Co., or standard chemical stoneware companies, manufacturers.

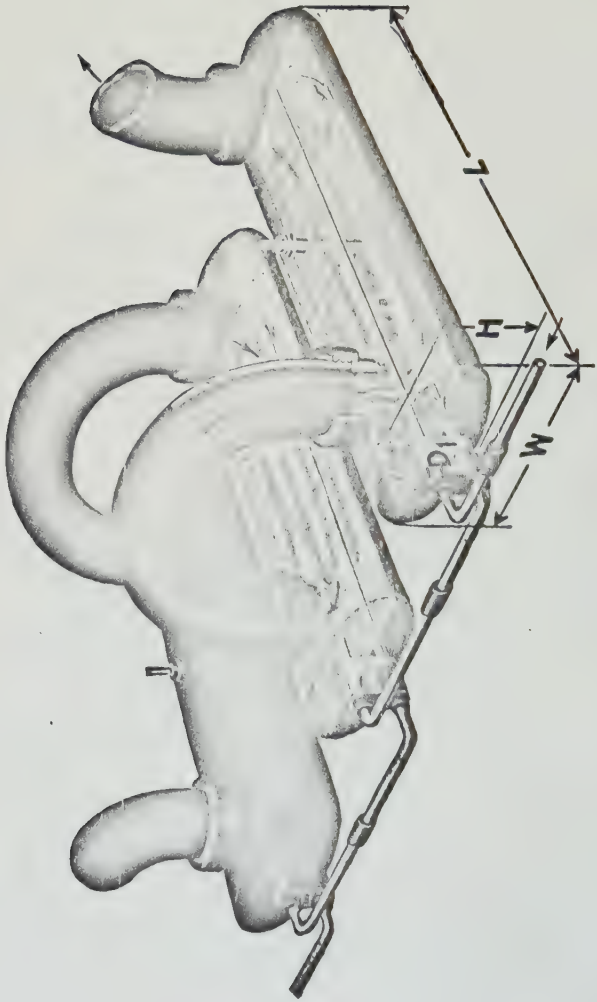

FIGURE 21.—Meyer absorbers.

This is made of fused silica,[7] so shaped as to carry a pool of acid. It is set up and water-cooled just as is an *S*-pipe gas cooler. The walls are thin and the vessel can be cooled over its whole surface so that it is much more effective than the corresponding area in the form of tourills but it is also more expensive to install for equivalent cooling capacity.

Attention has been given to cooling applied to the vessel in which absorption is being performed. Another method of applying cooling to the absorption system is to remove the absorbing acid and cool it by air or water and return it again to the absorbing vessel. This is being done with some of the vitreosil absorbers mentioned above and it forms an essential feature of all absorbing towers where the absorbing acid is necessarily kept in circulation. In the absorbing system used on the direct-fired rotary furnace, which is described below, the acid is circulated by means of pulsometers (Fig. 22), and no water-cooling is required except on the first tower and that only when the temperature of the cooling water and the air become so high in summer as to make it difficult to make 20-degree Baumé acid. In the latter case a stoneware coil submerged in water is made to form a part of the circulating system (Fig. 17), where it functions very effectively on the gas of this furnace which generally runs quite uniformly around five per cent hydrogen chloride. With reference to this method of cooling Cumming[8] states that "A series of scrubbers with the liquid passing counter-current against the gas current, and thoroughly efficient repeated cooling of the liquid, appears the only rational alternative to the old way of making towers big enough." Eagleson[9] describes a special installation of towers and coils of this character for cooling and absorbing.

Retorts that operate intermittently are classed with pot and muffle furnaces as regards cooling requirements, but with retorts that are run by the continuous method as well as with mechanical muffle furnaces (in both of which the gas is uniformly quite concentrated), it is generally necessary to apply water-cooling of the circulating

[7] Thermal Syndicate's Vitreosil.
[8] Lunge & Cumming, *Manufacture of Acids & Alkalies*, 1923.
[9] U. S. Pat. 1,563,732.

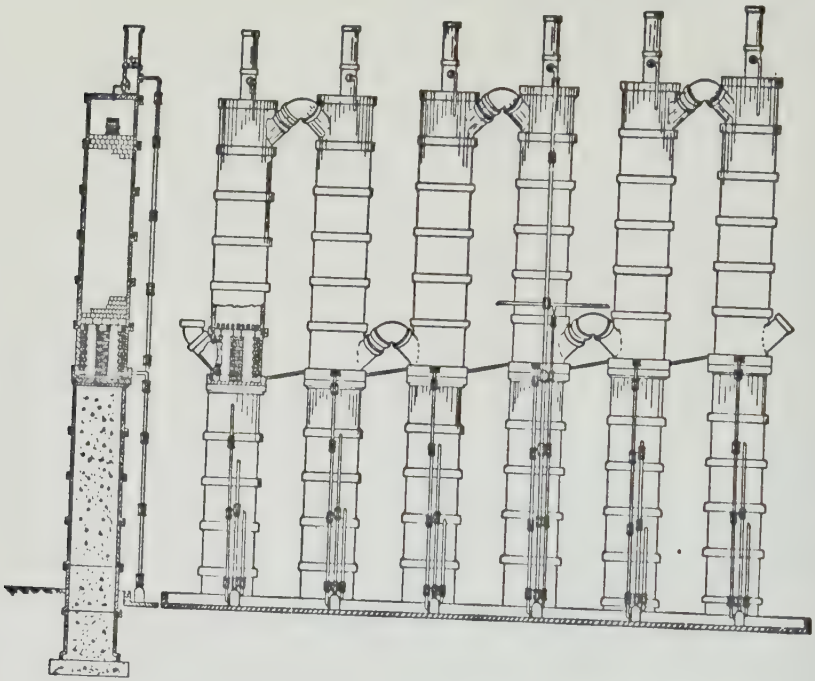

FIGURE 22.—Absorbing towers for direct-fired rotary absorbing system.

acid. A tower taking a stream of ten gallons of circulating acid a minute requires a coil with about twenty square feet of cooling surface.

Purification of the Gas

The gases from the pot side of a pot-and-muffle furnace as well as the gas from retorts are practically free from sulfuric acid, that is, the sulfuric acid in the hydrochloric acid made from this gas is well within the limit demanded by the trade. On the other hand, other furnace gases of any kind contain enough sulfuric acid to contaminate the product acid to the extent of making it unsuitable to the average consumer. Many users accept acid containing one-half of one per cent sulfuric acid, but the majority want it one tenth of one per cent or lower, so that apparatus for the removal of sulfuric acid from the gas before absorption is necessary in every

plant producing for general distribution. In the old plants the gas was taken from the furnace directly to a preliminary tower built of stone slabs where a good deal of the sulfuric acid condensed by air-cooling drained off separately. The slabs have grooved joints made up with asbestos rope and pitch and are held together with corner irons and heavy rods. They are six inches thick, so that the

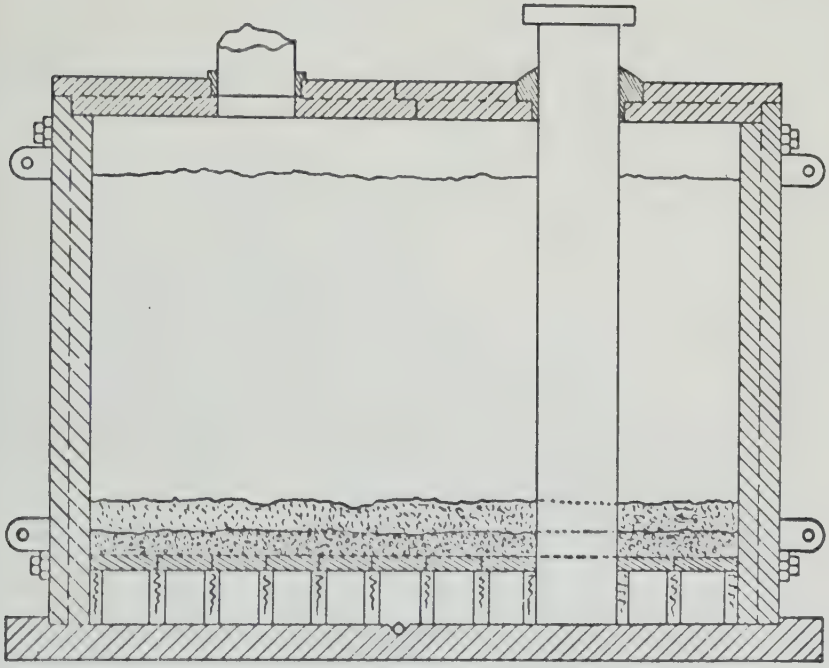

FIGURE 23.—Stone box filter.

towers are inefficient as coolers and even when placed at such a distance from the furnace as to be always cooled below the boiling point of weak sulfuric acid they do not remove the necessary amount of this acid. The reason for this is that the gas carries part of the sulfuric acid in the form of mist which can only be stopped by filtration through fine coke or by electrical precipitation. The former is the method in general use. The coke may be contained in a box made of stone slabs (Fig. 23). Cleveland or Ohio sandstone is used because it is very acid-resisting; granite also answers.

Sometimes the slabs are boiled in tar before assembling, but there is only slight penetration so that it is doubtful if the treatment is worth the expense. These stones sometimes crack under comparatively slight heating or other strain and they must then be replaced at considerable expense; cementing such cracks is seldom successful particularly in the case of the bottom slab. Preliminary towers and filters are sometimes built of acid brick set in silex and silicate of soda but they are not as tight or durable as the stone ones.

A cheaper and tighter filter which looks and stands up better is formed of the required number of short stoneware towers connected in parallel, as shown in Figure 17.

The necessary area for a hand-worked muffle delivering approximately 150 cubic feet of gas per minute is about 30 square feet with a 30-inch depth of fine coke. For other furnaces these proportions must accord with the volume of the gas. To be effective the gas must enter these filters at not much above 175° F. so that it is best to locate them after the *S*-pipe gas cooler. The temperature entering the filters must be regulated to prevent excessive condensation of acid because this filter acid must all be redistilled. It ordinarily contains about one-third each of sulfuric acid, hydrochloric acid and water. The quantity of this acid should be less than a hundred pounds per ton of product with properly regulated gas temperatures.

Absorption Equipment

Packed towers have been mentioned as the arrangement giving highest capacity per unit area or volume. They are also the cheapest to install relative to output and more durable and they also contain fewer joints, especially of the kind necessary to connect up the various forms of small absorbers. The area of liquid surface in a unit volume in a packed tower is many times greater than the area in what may be imagined as the corresponding volume in absorbers which have a comparatively quiescent pool of acid over which the gas passes.

Haslam, Ryan and Weber,[10] working with sulfur dioxide and water in a piece of 8-inch glass pipe 30 inches long, made interesting comparisons on absorption with a wetted wall, a fine spray, spiral

[10] *Trans. Am. Inst. Chem. Eng.* 15, I, 177.

ring packing and coke packing. Their results show that the capacity is highest for coke. They worked out equations connecting an absorption coefficient expressed in pounds per minute per cubic foot of volume per millimeter of mercury partial pressure difference, with gas velocity in feet per second, according to which coke packing has the highest absorbing capacity for increasing gas velocities.

In absorbing sulfur dioxide in water in large towers in a liquid sulfur dioxide manufacturing plant the author has observed that the same towers absorbed much more gas when packed with coke than when sprayed or brick packed.

Whitman and Davis [10] found that by passing a mixture of gas and air over the surface of a liquid being slowly agitated by a stirrer the absorption of sulfur dioxide in water was not so rapid as in the above experiment because the liquid film is thicker despite the agitation caused by the stirrer.

Zeisberg gives some comparisons of different tower-packing surface areas per cubic foot, etc. (see Table 19), but as he does not take into account the porosity of coke, the advantage of coke over noncellular material shown above is not apparent.

The distribution of the absorbent over the top of the tower must be uniform so that it is essential to have well-made stoneware distributors with numerous holes for admitting the liquid. Splash plates do not spray the whole surface and they sometimes get displaced, and automatically rotated tubes frequently plug up and stop. To admit a uniform stream at a constant head from a supply boot the usual movable syphon is used together with a float valve on the boot to regulate the overflow.

Figure 17 is a typical absorbing system for a pot-and-muffle-, retort-, mechanical muffle- or electrolytic plant. It consists of a fused quartz gas cooler in four parallel rows connected to four filters which deliver the cooled, sulfuric acid-free gas to the first or absorbing tower. This tower has a cooling coil in the circulating system. Water is introduced through the top of the second or scrubbing tower, from the bottom of which it flows to the first tower. The draft may be induced by a steam jet or a duriron,[11] stoneware [12] or

[11] Duriron Co., New York.
[12] General Ceramics Co., New York.

rubber-lined fan. All of the gas from the generators mentioned runs about 30 per cent hydrogen chloride, fairly constantly, excepting that from the pot-and-muffle furnace. The water entering the scrubbing tower may be set at a constant rate to correspond to the strength of product desired, where the gas concentration does not change, but it must be varied to suit the changing amount of hydrogen chloride from the pot-and-muffle furnace. The strength of the acid at the outlet of the scrubbing tower is usually about 13° Bé. This is about the concentration of constant-boiling acid; if the acid is stronger, then the tower is acting as an absorber as well as a scrubber and the loss through the exit may increase. If the acid is weaker, it should scrub out practically all of the hydrogen chloride, providing the volume of gas is not too great and the water is uniformly distributed over the surface of the coke at the top. Distributors, not visible in the illustration, are provided for this purpose under the tower tops. The quantity of water added to the tower is not large in proportion to the area to be covered. Much better scrubbing and distribution of the absorbent and lower exit gas results if the scrubbing acid is circulated over the tower. When this is done, however, it is very important that the strength be kept below 13° Bé.

These two towers with a diameter of 40 inches and a 12-foot depth of egg size coke packing will absorb all of the hydrogen chloride from about 300 cubic feet of gas per minute of a concentration of approximately 30 per cent hydrogen chloride. Of course, this concentration may be increased if sufficient cooling is provided but if the gas velocity is much greater, then additional scrubbing is required. A velocity of one foot per second in the towers gives good absorption without excessive resistance. The resistance of two towers apparently packed alike may vary considerably. In the above case the drop in pressure in each tower may be from one- to three-eighths of an inch of water.

It has been mentioned that acid made from electrolytic chlorine is the purest of the commercial grades. In this process there is no source of contamination by the distillation of iron chloride and care is taken against picking up iron in absorption, accordingly it is customary to use only fused silica. Figure 18 illustrates such a plant.

TABLE 19.—*Packing materials for hydrochloric acid absorptions towers (Zeisberg).*

Packed	Multiply constants by 10^{-4}									* % free space	Surface sq. ft. per cu. ft.	Wt. lbs. per cu. ft.	No. units per cu. ft.
	f_d^d	f_w^d	f_c^d	f_d^s	f_w^s	f_c^s	f_d^p	f_w^p	f_c^p				
Quartz, 6"	58	60	60	...	...	...	...	...	...	44	6.3	89	...
Quartz, 3"	101	110	139	...	...	...	...	...	...	46	12.7	86	...
Coke, 3"	76	81	94	...	...	...	...	...	...	58	12.7	29	...
3" x 3" Hood's corrugated diaphragm rings	51	56	63	31	42	58	26	28	28	65(1)	24.0	48	53
										57(2)	30.0	61	67
										55(3)	31.0	63	70
3" x 3" Hood's "Chemico" corrugated spiral rings	45	54	63	54	54	61	...	...	...	72(1)	22.0	40	48
										64(2)	29.0	53	63
6" x 6" Hood's "Chemico" corrugated spiral rings	...	...	...	38	47	50	24	31	35	58(2)	15.0	53	8
										58(3)	15.0	53	8
6" Hood's corrugated Hech blocks	16	36	36	35	38	38	26	28	28	72(1)	10.7	39	4.2
										62(2)	14.3	52	5.6
										62(3)	14.3	52	5.6
Brick on edge, staggered, 8x2¼x3¾	...	...	...	...	...	...	31	33	35	55	11.6	68	17.5
Tile on edge, staggered, 8x4x1½	...	...	...	...	...	...	43	43	74	45	14.0	81	21

(1) dumped. (2) stacked. (3) packed. * % free space—is percentage of total volume of tower.

Since the constants shown above in tabular form, together with other characteristics of various types of packing, will be unintelligible without explanation, it is desirable to give some attention to the theoretical considerations involved.

Assuming that the general law of the flow of fluids holds in this case (this was experimentally demonstrated to be true), the frictional resistance is proportional to the square of the velocity of flow. This resistance may be expressed as the pressure necessary to produce the given flow.

Let s = linear velocity in feet per minute;
p = pressure in inches of water;
k = a frictional constant;
a = area of cross-section of packing in square feet;
h = height of packing in feet;
v = volume of air passing in cubic feet per minute.

Then

$$p = ks^2 \quad \ldots\ldots\ldots (1)$$

and

$$s = \frac{v}{a} \quad \ldots\ldots\ldots (2)$$

Therefore

$$p = \frac{kv^2}{a^2} \quad \ldots\ldots\ldots (3)$$

Since the resistance, or the pressure, varies directly as the height of the packing, we may hence write

$$p = \frac{khv^2}{a^2} \quad \ldots\ldots\ldots (4)$$

However, k is a general constant, varying in value with the type of packing. We have therefore designated f as the frictional coefficient of one square foot of packing one foot high, and may write equation (4) as

$$p = \frac{fhv^2}{a^2} \quad \ldots\ldots\ldots (5)$$

"f" of course differs for each style of packing, with its method of disposal in the tower and with the amount of liquid circulating in the tower. In order to make f more descriptive, superscripts and subscripts have been added, as follows:

f^d = packing dumped into tower;

f^s = packing stacked, i. e., arranged regularly in layers, but with no attempt to have pieces in one layer in any way related to those in adjacent layers;

f^p = packing packed, i. e., arranged regularly in layers, with the axes of pieces in adjacent layers coinciding;

f_d = packing dry;

f_w = packing wet with water but drained as completely as possible;

f_c = packing with water circulating over it at a rate of 11 lbs. per square foot cross-sectional area per minute.

It is, of course, evident that we may have, for example f_d^d = packing dumped and dry, and that quartz, coke, etc., can give values only for f^d, and not for f^p, or f^s.

If no scrubbing tower is used there must be a considerable exit loss but if the usual construction of stoneware and coke or brick or ring packing is used then the advantage of iron-free fused silica absorbers is not so great. This matter of iron contamination is not so important for commercial acid in general because acid made in the usual towers rarely contains iron in objectionable quantity. Ordinary commercial electrolytic acid runs 0.001 per cent iron, and acid made from salt and sulfuric acid or from salt and sodium bisulfate in any type of furnace runs close to 0.02 per cent iron.

Fritz and Withrow [13] have determined by experiment with vitreosil absorbers of standard sizes the absorption per square foot with different gas concentrations; their results are shown in Table 20. In this investigation the absorption system was studied from the standpoint of constant production of acid of a desired concentration in as small an absorption area as possible. The gas velocities were very low, ranging from 2.18 feet per minute for a

TABLE 20.—*Absorption of hydrogen chloride in Vitreosil absorbers.**

Concentration of entering gas, in per cent by volume of HCl.	97	68	68	47	25	13
Absorption area, square feet ..	3.08	3.52	3.97	4.66	6.44	7.47
Acid made, in pounds	88	110	110	89	89	90
Specific gravity of product at 20° C.	1.180	1.152	1.152	1.175	1.175	1.175
Production of acid of sp. g. 1.175 at 20° C., in pounds per hour per square foot of absorption surface	4.89	4.37	4 08	3.18	2.30	2.00
HCl gas absorbed, in pounds per square foot per hour	1.7071	1.5081	1.4243	1.1101	0.8029	0.6982
HCl gas absorbed under standard conditions, in cubic feet per square foot per hour	16.729	14.779	13.958	10.879	7.868	6.842

Average pressure in system, ¼ inch under barometer.
Absorption area, 12.20 sq. ft.
Average temperature of entering gases, 25° C.
Average temperature of input feed water, 28° C.
Average temperature of output acid, 37° C.
Average temperature of input cooling water, 10.5° C.
Average temperature of output cooling water, 13.5° C.

* Fritz and Withrow, *Trans. Am. Inst. Chem. Eng.*, **15**, I, 217.

[13] *Trans. Am. Inst. Chem. Eng.* **15**, I, 217 (1923).

94 per cent gas to 15.77 feet for a 13 per cent gas, calculated at 0° C. and 760 mm. In retort and electrolytic plants the gas velocities are low and the data for absorption per unit area are comparable to these, but in pot-and-muffle plants where the velocity may be 75 feet per minute the absorption per unit area is much lower.

Figure 22 is an absorbing and scrubbing set for a direct oil-fired rotary furnace receiving 1,000 cubic feet of 5 per cent hydrochloric acid gas per minute. Every tower is equipped with a pulsometer running at the rate of 10 gallons per minute. This gas is too weak to make 22° Bé. acid but 20° Bé. acid can be turned out steadily. It is connected with a gas cooler and coke filter and a duriron fan is used to produce the draft. The towers are 15 feet high and 40 inches in diameter and are packed with spiral rings. The hydrogen chloride in the exit gas runs under 0.0005 gram per liter with little variation. The foundation of the towers consists of a substantial footing on which sewer tile of the same diameter as the towers or a little greater are placed and then filled with concrete.

Cementing Joints. Joints in chemical stoneware and fused silica gas lines and towers, which are all of the bell and spigot style, are made up first by working down firmly with a flat stick a course of asbestos rope to form a foundation for the cement. The best cement is made by melting pitch and stirring in powdered china clay or barium sulfate or similar inert material to give it a body. A small amount of short-fibered asbestos improves it some. If the cement is to be used on cold joints some coal tar should be added to make it softer. If a little care is taken in making this mixture to suit it to the temperature of the joint a very permanent and tight job may be obtained. Molten sulfur may be poured in on top of the asbestos instead of cement; it makes a neat tight job but the ware is apt to be broken when it is desired to take it apart.

Other Methods of Absorption and Purification

Solvay [14] proposed to concentrate hydrogen chloride in weak gas by absorption in calcium chloride solution with recovery by distillation and also the recovery of hydrogen chloride from dilute

[14] U. S. Pats. 240,196 and 453,986.

aqueous solution by mixing with sulfuric acid or calcium chloride and distilling. DeHaen [15] has a similar method.

Lasher [16] patented an apparatus for absorbing hydrogen chloride, which consists of a chamber containing weak hydrochloric acid with partly submerged baffles under which the gases are forced.

Frederichson [17] has patented a process of redistillation and fractional condensation intended for making C.P. acid. Kipp and Hoff [18] accomplish the distillation of hydrochloric acid by passing an alternating current through electrodes immersed in the acid.

Schmidt [19] claims advantages in the removal of arsenic from hydrochloric acid by means of activated carbon. Hasenbach [20] removes arsenic from hydrochloric acid by washing with mineral oil and Wylde and Kynaston [21] remove arsenic from hydrogen chloride gas by mixing it with a little chlorine and passing it through coke. The removal of arsenic is of little interest nowadays because only arsenic-free raw materials are used to make hydrochloric acid.

For the removal of chlorine from hydrochloric acid Skinner [22] has patented a method of distilling and treating with hydrocarbon gas.

[15] U. S. Pat. 687,994.
[16] U. S. Pat. 1,337,141.
[17] U. S. Pat. 1,398,224.
[18] U. S. Pat. 1,507,120.
[19] U. S. Pat. 1,571,648.
[20] U. S. Pats. 834,977 and 862,906.
[21] U. S. Pat. 605,369.
[22] U. S. Pat. 875,558.

Chapter IX

Economic Factors—Production Costs, Handling and Shipping

Plant Site

The location of the plant should be chosen with regard chiefly to the fact that no hydrochloric acid plant, however perfect, is a good neighbor. In moist weather, the gas from warm salt cake, storage tanks and the plant exit, however slight, is sufficient to generate a fog which spreads to adjoining buildings.

Choice of Equipment

Only exceptionally does it pay to manufacture hydrochloric acid in small quantities; for example, when it is to be used as a gas, and even here unless the amount is fairly large it is best to generate the gas by distilling commercial 20° Bé. acid with strong sulfuric acid. The retort is the least expensive plant to build but for independent operation its usefulness is restricted to distant places where shipping is high or where gaseous hydrogen chloride is required in sufficient quantity; the by-product bisulfate in such cases is usually thrown away.

To manufacture for sale, if nitre cake is available as a raw material, by far the most economical equipment is a mechanical furnace. Next to this is the combination of a retort and mechanical furnace. If nitre cake is used there is produced over two tons of salt cake to one ton of hydrochloric acid, while if salt and acid are the raw materials more acid than salt cake is made so that the demand for these products largely determines the type of plant.

It is hard to imagine any situation that would justify the installation of a pot-and-muffle furnace. They are not well adapted to the use of nitre cake; they require a relatively large absorbing system

because of their intermittent operation; and it is difficult to get men to work them.

There are several points bearing on the choice between a Mannheim or other make of mechanical muffle furnace and the internally-fired rotary furnace; the salt cake from the former is inferior but on the other hand it delivers a gas that is strong enough to make 22° Bé. acid whenever that is desired; an all-iron Mannheim furnace can be run on salt and acid directly which is sometimes convenient but rarely necessary; it requires a smaller absorbing system than the rotary furnace does with its weaker gas but this is more than compensated for by the lower cost of the rotary furnace on the basis of unit production.

Construction and Operating Costs

The data given in Tables 21 and 22 are based on the operation of single units of standard size; that is, the pot-and-muffle furnace takes 8 charges of 1,000 pounds of salt in twenty-four hours and is worked by two men a shift, who look after the absorbing system; the Mannheim furnace is an 11-foot diameter all-iron muffle furnace run by one man with three men on the day shift to crush and mix nitre cake and salt; the rotary furnace gang is taken at three 24-hour men and six day men crushing and mixing the nitre cake and salt. The furnace is the standard 6-foot diameter by 22 feet long.

The plant costs are approximate present day estimates made on the same basis for comparison. No buildings, conveyors or tramways are included but just the actual equipment in place with feeding mechanism, oil-burning outfit and all motors and drives.

TABLE 21.—*Initial cost of three types of hydrochloric acid plants compared.*

Type of Furnace:	Pot-and-Muffle	Mannheim	Rotary
Cost:			
Furnace (complete)	$ 8,000	$15,000	$12,000
Absorbing system	6,500	6,500	11,500
Total	$14,500	$21,500	$23,500
Tons of products per 24 hours (20° Bé. acid and salt cake)	12	12	36
Cost on basis of ton-day of products	$ 1,200	$ 1,800	$ 653

TABLE 22.—*Operating costs of three types of hydrochloric acid plants.*

Type of Furnace	Pot-and-Muffle	Mannheim	Rotary
	Per ton of products	Per ton of products	Per ton of products
Operating costs:			
Labor, 45¢ per hour	$ 2.00	$1.90	$1.70
Maintenance	1.00	1.25	1.00
Power	.15	.44	.40
Fuel (coal $5 per ton)	1.25	.63	....
Oil (5¢ per gallon)	....	....	.40
Overhead	.50	.50	.30
Depreciation, interest, taxes (10 per cent)	.33	.50	.20
Salt ($8 per ton)	2.66	1.66	1.66
Sulfuric acid, 60° Bé. ($10 per ton)	2.37	....	....
Nitre cake ($5 per ton)	....	2.61	2.61
Total operating cost	$10.26	$9.49	$8.27

The labor item appears high on the mechanical furnaces but about half of it is spent in crushing and mixing nitre cake and salt. The pot-and-muffle furnace, using salt and acid, shows up to advantage in this respect but this difference disappears when the mechanical furnaces are fed molten nitre cake direct from hydrochloric or nitric retorts.

It is not necessary to house the towers and filters. The furnace buildings are made of brick or of wood protected with creosote or bituminous paint.

Pumping. Pulsometers are mentioned on page 106 and shown in Figures 17 and 22. They easily lift 15 gallons of 20° Bé. acid per minute over a net elevation of 15 feet with 20 pounds of air. They will of course lift much higher but this is mentioned as approximately the height at which glass lines, jointed with soft rubber sleeves, are giving good service. They are made of chemical stoneware in only one size. Acid eggs made of the same material are useful for handling small quantities in special cases. These eggs are built for hand operation and also for automatic running. Centrifugal pumps are convenient for circulating acid on towers or for loading tank cars, but more particularly the latter because of

their large capacity. Pumps are made of chemical stoneware,[1] hard rubber,[2] rubber lined cast iron,[3] and duriron.[4] The first is rather fragile, the next two give good service with cold acid, while the last stands up very well against warm acid, although it is not completely resistant to it.

Storage. The best storage tanks are made of three-inch wood staves held with round iron and lined with soft sheet rubber. The work of placing the sheets and vulcanizing the joints is done by men furnished by the rubber companies, several of which do these jobs.[5] The staves are painted with creosote before assembling and sometimes an inner wood lining of $\frac{7}{8}$ inch clear matched pine 2 inches wide is put in. This is covered with a canvas lining which is tacked on and the pure rubber sheets $\frac{3}{32}$ inch thick are cemented on the canvas. These tanks remain tight for years if care is taken to protect the lining from injury by syphons or otherwise. The tanks should have reasonably tight covers made of creosoted plank. A tank of this kind of 25-ton capacity will cost about $1,800.

A very good style of storage, but an expensive one, is a series of stoneware jars, each of about 500 gallons capacity. They are placed in line and connected by syphons so that the acid can all be drawn out at one point. These cost about 30 per cent more per ton of storage capacity than a 25-ton rubber-lined wood tank.

Before the advent of rubber linings, tanks were built of wood and lined in various other ways. These jobs depended largely on workmanship and quality of cements used but sooner or later they all leaked and required frequent overhauling. The simplest and generally the best was a tank 14 feet in diameter and 8 feet high, built of selected close-fitting 3-inch thick staves held together with 10 one-inch round iron hoops, to which when dry two coats of a primer [6] were applied cold. Before the primer quite dried three coats of Hermastic cement [6] were put on. This cement was first heated gradually to its melting point, about 280° F., but no higher,

[1] General Ceramics Co.
[2] American Hard Rubber Co.
[3] Oliver Continuous Filter Co.
[4] Duriron Co.
[5] U. S. Rubber Co., Goodyear Rubber Co., Miller Rubber Co. and others.
[6] American Bitumastic Enamels Co., Chicago, Ill.

as bubbles then occurred which later caused leaks. Tanks were sometimes lined with acid brick over the bottom and sides, the side brick being laid flat and one inch away from the staves. Ordinary cement was used for laying the brick but only enough was taken to leave the joints empty about half way across. Molten sulfur was then poured into the space between the staves and the brick so that it completely filled it and penetrated between the brick, and while the sulfur on the side was still molten a layer one inch deep was poured over the brick floor. A mixture of three parts pitch and one part tar was sometimes used in place of sulfur. Storages were also built up of one heavy circular wood tank within another with

FIGURE 24.—Rubber-lined steel tank car.

a two-inch annular space between, which was filled with the above tar and pitch mixture. A great deal of acid is stored in carboys but that is much more expensive than bulk storage when the deterioration of the carboys is taken into account.

Shipping. When it is considered how much attention over so many years has been given to devising a package for shipping one or two hundred pounds of hydrochloric acid, it must be concluded that the present glass carboy which accords with Interstate Commerce Commission specifications and tests is a pretty good thing after all, in spite of its numerous shortcomings. The need seems to be to substitute for glass a material less fragile and equally resistant to corrosion. Rubber-lined steel barrels have appeared but they have not been adopted yet.

The development of tank cars has paralleled that of storage tanks and several kinds are in current use. Figure 24 is a rubber-lined

steel tank and Figure 25 is a series of transversely placed wooden tanks also rubber-lined. A long familiar type is a longitudinal steel tank containing a wooden tank and heavy pitch inter-lining. These various cars carry from thirty to fifty tons and cost from $4,000 to $5,000.

A very serviceable tank for motor truck shipments is now made of quarter-inch welded steel, lined with rubber. It has a capacity of six tons and costs $750.

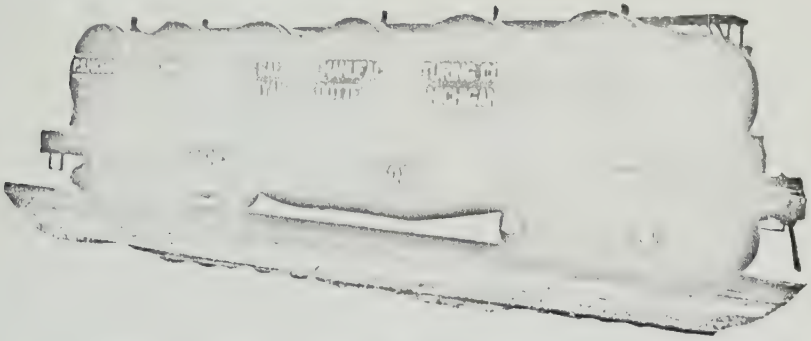

FIGURE 25.—Tank car with rubber-lined transverse wood tanks.

Handling Liquid Hydrogen Chloride.—Hydrogen chloride belongs to the class of easily liquefiable gases like chlorine and sulfur dioxide. In the liquid form it is no more corrosive to iron than they are, so that it can be handled in just about the same way. It can be liquefied in all-iron compressors like sulfur dioxide or by means of a falling column of strong sulfuric acid as for chlorine and it could be shipped in like manner in cylinders or in Class *V* tank cars. It has not been done on a large scale and it is possible that some unforeseen difficulty might develop but no doubt a cheap and practicable way will be found when economic conditions make it appear profitable.

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